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# **MELT GROWN GERMANIUM SINGLE CRYSTALS BY AXIAL HEAT PROCESSING METHOD**

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Successful processing of homogeneous semiconductor single crystals from their melts depends strongly on precise control of thermal and fluid flow conditions near the solid/liquid interface. In contrast with the stabilizing influence of axial temperature gradients, radial temperature gradients create non-planar interfaces that in turn contribute to convection in the liquid and radial segregation of the dopant. In this project, we utilize a novel crystal growth technique called Axial Heat Processing (AHP) that uses a baffle, positioned inside the melt near the interface, to supply and/or conduct heat axially. The baffle promotes more stable and planar growth, as well as reducing convection. The latter is because the baffle reduces the aspect ratio of the melt as it separates the melt into three sections, above the baffle, in the feed gap between the baffle and the crucible wall, and between the interface and the baffle base. The presentation addresses the influence of melt height and growth velocity on the segregation profile of AHP-grown Sb doped Ge single crystals.

**Keyword: characterization**

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***ID#: 2***

**Vibrations and g-Jitter: Transport Disturbances Due to Residual Acceleration During  
Low Gravity Directional Solidification Experiments**

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CWRU

Abstract in Progress

**THE EVOLUTION OF DENDRITE MORPHOLOGY DURING ISOTHERMAL COARSENING****J. Alkemper\*, D. Kammer, and P.W. Voorhees**

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Dendrite coarsening is a common phenomenon in casting processes. From the time dendrites are formed until the inter-dendritic liquid is completely solidified dendrites are changing shape. These changes in shape are driven by variations in interfacial curvature along the dendrite and the resulting in a reduction of total interfacial area. During this process the typical length scale of the dendrite can change by orders of magnitude and the coarsening process in large part determines the final microstructure. Dendrite coarsening is thus crucial in setting the materials parameters of ingots and of great commercial interest.

This coarsening process is being studied in the Pb-Sn system with Sn-dendrites undergoing isothermal coarsening in a Pb-Sn liquid. Results are presented for samples of approximately 50% dendritic phase, which have been coarsened for different lengths of time. Presented will be several three-dimensional microstructures obtained by serial-sectioning and an analysis of these microstructures with regard to interface orientation and interfacial curvatures. This shows the evolution of not only the microstructure itself, but also of the underlying driving forces of the coarsening process. In order to visualize the link between the microstructure and the driving forces we will present a three-dimensional microstructure with the interfaces colored according to the local interfacial mean curvature.

**Keywords: dendrite coarsening, serial sectioning, interfacial curvature, characterization**

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## **FLOW VISUALIZATION OF LOW PRANDTL NUMBER FLUIDS USING ELECTROCHEMICAL MEASUREMENTS**

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It is well established that residual flows exist in contained liquid metal processes. In 1-g processing, buoyancy forces often drive these flows and their magnitudes can be substantial. It is also known that residual flows can exist during microgravity processing, and although greatly reduced in magnitude, they can influence the properties of the processed materials. Unfortunately, there are very few techniques to visualize flows in opaque, high temperature liquid metals, and those available are not easily adapted to flight investigation.

In this study, a novel technique is developed that uses liquid tin as the model fluid and solid-state electrochemical cells constructed from Yttria-Stabilized Zirconia (YSZ) to establish and measure dissolved oxygen boundary conditions. The melt serves as a common electrode for each of the electrochemical cells in this design, while independent reference electrodes are maintained at the outside surfaces of the electrolyte. By constructing isolated electrochemical cells at various locations along the container walls, oxygen is introduced or extracted by imposing a known electrical potential or passing a given current between the melt and the reference electrode. This programmed titration then establishes a known oxygen concentration boundary condition at the selected electrolyte-melt interface. Using the other cells, the concentration of oxygen at the electrolyte-melt interface is also monitored by measuring the open-circuit potentials developed between the melt and reference electrodes. Thus the electrochemical cells serve to both establish boundary conditions for the passive tracer and sense its path.

Rayleigh-Bénard convection was used to validate the electrochemical approach to flow visualization. Thus, a numerical characterization of the second critical Rayleigh numbers in liquid tin was conducted for a variety of Cartesian aspect ratios. The extremely low Prandtl number of tin represents the lowest value studied numerically. Additionally, flow field oscillations are visualized and the effect of tilt on convecting systems is quantified.

Experimental studies of the effect of convection in liquid tin are presented. Three geometries are studied: (1) double electrochemical cell with vertical concentration gradients; (2) double cell with horizontal concentration gradients; and (3) multiple cells with vertical temperature gradients. The first critical Rayleigh number transition is detected with geometry (1) and it is concluded that current measurements are not as affected by convection as EMF measurements. The system is compared with numerical simulations in geometry (2), and oscillating convection is detected with geometry (3).

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**Keywords: solid electrolytes, flow visualization, convection**

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## COUPLED GROWTH IN HYPERMONOTECTICS

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Many immiscible alloy systems show promise for use in engineering applications such as superconductors, high performance permanent magnets, electrical contact materials and filters for medical applications. However, aligned fibrous microstructures are required in order to take advantage of the desirable characteristics of the alloys. The establishment of coupled growth conditions in hypermonotectic alloys through directional solidification can lead to the formation of the desired fibrous composite-like microstructure where solute-rich fibers form in a matrix composed of nearly pure solvent.

The overall objective of this project is to obtain a fundamental understanding of the physics controlling coupled growth in hypermonotectic alloys. The investigation involves both experimentation and the development of a model describing solidification in monotectic systems. The experimental segment is designed to first demonstrate that it is possible to obtain interface stability and steady state coupled growth in hypermonotectic alloys through microgravity processing. This segment will also permit experimental determination of the limits of interface stability and the influence of alloy composition and growth rate on microstructure. The objectives of the modeling segment of the investigation include prediction of the limits of interface stability, modeling of convective flow due to residual acceleration, modeling of solute redistribution, and determination of the influence of surface tension driven flows at liquid-liquid interfaces.

Unfortunately, control of the solidification process in hypermonotectic alloys in order to produce the required microstructures is very difficult. Study of the solidification process on Earth is hindered by the inherent flows that occur in these systems and by the possibility of the heavier of the two immiscible liquid phases settling during processing. In order to permit solidification under the conditions necessary to form aligned fibrous structures in these systems, experimentation must be carried out under low-gravity conditions.

Preliminary flight experiments carried out during the LMS mission provided encouraging results on the ability of microgravity conditions to promote coupled growth in hypermonotectic alloys. This presentation will compare the microstructures and compositional uniformity of flight samples with control samples solidified under unit gravity conditions. Ground based processing results in axial composition variations due to convective mixing. However, modeling of the solute redistribution in hypermonotectics has not been reported in the literature. It will be shown that proper selection of parameters leads to a simple solute redistribution relationship of familiar form.

**Keywords:** immiscible alloys, hypermonotectics, monotectics, flight samples, directional solidification

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**SELF-DIFFUSION IN LIQUID ELEMENTS:  
CONVECTIVE EFFECTS DURING DIFFUSIVITY MEASUREMENTS  
IN LIQUIDS WITH AN APPLIED MAGNETIC FIELD**

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During liquid self-diffusion experiments, a small non-uniformity in temperature within the melt may drive a buoyant convection in the presence of gravity or even with residual acceleration magnitudes characteristic of microgravity conditions. This convection can result in erroneous values of the measured diffusivity. Alexander et al. [1] showed that for three-dimensional (3D) time-dependent transport in the presence of gravity with horizontal temperature non-uniformities across the sample as low as 1 and 0.1 K, convective transport rates in 1 and 3 mm diameter capillaries, respectively, can exceed diffusive transport rates, and, thus, result in higher values of measured diffusivities. However, while considerable scatter (up to 100%) occurs in diffusivity values, the available data seems to suggest that numerical modeling overemphasizes the effect of convective transport. The purpose of this paper is to quantitatively estimate the magnitude of allowable temperature non-uniformities in the liquid that will insure that measured diffusivity is within 5% of the actual value when the experimental system is subject to magnetic field.

We employ a basic, two-dimensional axisymmetric, model. A steady, uniform heat flux that produces a radial temperature difference in the liquid is imposed on the sidewall of the cylindrical container while uniform heat losses are imposed on the top and bottom walls. Then, a steady, spatially-periodic heat flux is superimposed on the sidewall of the cylinder to predict the effect of spatial temperature variations which represent the localized hot and cold spots along the sidewall. Simulated diffusivity results for two different initial conditions with several different magnetic field strengths and five various temperature profiles along the sidewall are presented.

Time-dependent concentration is solved for various values of the mass Peclet number,  $Pe$ , (the ratio between the convective transport rate and the diffusive transport rate) and different magnetic<sup>m</sup> field strengths represented by the Hartmann number  $Ha$ . Diffusivities are obtained using the same algorithm used to extract diffusivity values from the actual experimental data [2]. The numerical results suggest that an additional periodic flux, or “hot” and “cold” spots, can significantly decrease the convective contamination in our geometry. The number of periodicity in temperature does not have a significant impact on the diffusivity results.

1. J. I. D. Alexander, J.-F. Ramus, and F. Rosenberger, *Microgravity Sci. Tech.* **9**: 158 (1996).
2. L.B. Jalbert, R.M. Banish and F. Rosenberger, *Physical Review E.* **57**: 1727 (1998).

**Keywords: self-diffusivity, convection, magnetic fields, thermal asymmetries, flight**

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# THERMOPHYSICAL PROPERTIES OF TE-BASED II-VI SEMICONDUCTORS: REDUCED ALGORITHMS FOR THERMAL DIFFUSIVITY DETERMINATION

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The determination of the thermal diffusivity  $\kappa$  (or conductivity  $k$ ) typically requires precise knowledge of the applied parameters. Such parameters include the time at which a heat pulse was applied, the amount of energy added or the initial temperature increase. The diffusivity is then obtained by matching the experimentally measured profile to the output of an analytical/numerical model. The resulting diffusivity is sensitive to values of these applied parameters.

This paper presents a methodology for measuring the thermal diffusivity using the difference between the temperatures measured at two locations. A heat pulse is applied for an arbitrary time to one region of the sample; either the inner core or the outer wall. Temperature changes are then monitored versus time. The thermal diffusivity is calculated from the temperature differences versus time. No initial conditions are used directly in the final result. The technique is applicable to liquids as well as to the solids tested here, provided of course that heat transport by convection is relatively negligible.

We consider a perfectly insulated circular cylinder under conditions for which the temperature depends only on the cylindrical radius  $r$ . The analytical solution has been derived for two initial temperature distributions. The first case is when an initial temperature distribution is set in the central portion of the sample. The second case is when a transient pulse heats the outer radius of the sample.

The resulting analytical equations can be simplified, i.e., eliminating the  $n=2$  and  $n=3$  terms, by selecting unique values for the central heated region and the measurement locations. Taking the logarithm of the temperature difference at two locations leads to an equation of the form, for both cases,

$$\ln(\Delta T_{ij}) = \ln(\beta_{ij}) - \left(\frac{\kappa \mu_1^2}{a^2}\right)t \quad (5)$$

Details of all of the initial conditions, including the initial applied temperature  $T_0$ , or the flux  $Q''$ , are contained in  $\beta_{ij}$ . Therefore, the slope of a plot of  $\ln(\Delta T)$  versus  $t$  is independent of the details of the initial conditions and is proportional to the value of  $\kappa$ , with a<sup>1</sup> known proportionality constant.

**Keywords:** thermal diffusivity, thermal conductivity, flight

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**ID#: 8**

## **INVESTIGATION OF THE RELATIONSHIP BETWEEN UNDERCOOLING AND SOLIDIFICATION VELOCITY OF NICKEL AND TITANIUM ALLOYS**

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The primary objective of this research is to reconcile differences between experimental measurements of solidification velocity as a function of undercooling and theoretical predictions. The theory proposed by Boettinger, Coriell, and Trivedi (BCT theory) has been one of the most widely used models for describing the nature of the solidification velocity of undercooled metal systems but fails to fit experimental results, particularly at undercoolings greater than 10% of the melting point. Additionally, in numerous ground-based research efforts there is considerable data scatter both within a given work as well as disagreement between different experimenters.

Solidification of undercooled melts in electromagnetic levitation and determination of solidification velocity using high speed thermal imaging systems are well established experimental techniques at Vanderbilt University. Containerless processing using electromagnetic levitation allows for the investigation of the full range of undercoolings, while direct thermal imaging reveals the true nature of solidification along the surface of a sample including the nucleation point and solidification path. These techniques yield accurate and reproducible results.

The solidification velocity of Ni-Ti, Ni-Sn, Ni-Si, Ti-Al, and Ti-Ni alloys was measured as a function of undercooling. It was observed that a solidification velocity plateau exists in intermediate undercoolings as a direct result of the addition of alloying elements. This behavior can be modeled with a Boltzmann logistic function. The logistic function can be used as a stand-alone model or incorporated in the BCT model to predict intermediate plateaus in the solidification velocity data.

**Keywords: solidification velocity, undercooling, containerless processing, electromagnetic levitation, new research**

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# **FREE DENDRITIC GROWTH OF SUCCINONITRILE-ACETONE ALLOYS WITH THERMOSOLUTAL MELT CONVECTION**

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A stagnant film model of the effects of thermosolutal convection on free dendritic growth of alloys is developed, and its predictions are compared to available earth-based experimental data for succinonitrile-acetone alloys. It is found that the convection model gives excellent agreement with the measured dendrite tip velocities and radii for low solute concentrations. However, at higher solute concentrations the present predictions show some deviations from the measured data, and the measured (thermal) Peclet numbers tend to fall even below the predictions from diffusion theory. Furthermore, the measured selection parameter is significantly above the expected value of 0.02 and exhibits strong scatter. It is shown that convection is not responsible for these discrepancies. Some of the deviations between the predicted and measured data at higher supercoolings could be caused by measurement difficulties. The systematic disagreement in the selection parameter for higher solute concentrations and all supercoolings examined, indicate that the theory for the selection of the dendrite tip operating state in alloys may need to be reexamined.

**Keywords:** dendritic growth, alloys, succinonitrile, convection, flight

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**PHASE-FIELD SIMULATIONS OF CONVECTION EFFECTS IN TWO- AND  
THREE-DIMENSIONAL DENDRITIC GROWTH**

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Convective effects on free dendritic crystal growth into a supercooled are investigated using the phase-field method. The phase-field model incorporates both melt convection and thermal noise. The flow calculations are performed using a multigrid SIMPLER algorithm in two dimensions and a finite element method in three dimensions. A multiple time step algorithm is developed that uses a large time step for the flow field calculations while reserving a fine time step for the phase-field evolution.

In two dimensions, the operating state (velocity and shape) of a dendrite tip in a uniform axial flow is found to be in quantitative agreement with the prediction of the Oseen-Ivantsov transport theory if a tip radius based on a parabolic fit is used. Furthermore, using this parabolic tip radius the ratio of the selection parameters without and with flow is shown to be close to unity, which is in agreement with linearized solvability theory for the ranges of the parameters considered. Dendritic sidebranching in a forced flow is also quantitatively studied. Compared to a dendrite growing at the same supercooling in a diffusive environment, convection is found to increase the amplitude and frequency of the sidebranches. The phase-field results for the scaled sidebranch amplitude and wavelength variations with distance from the tip are compared to linear WKB (Wentzel-Kramers-Brillouin) theory. It is also shown that the asymmetric sidebranch growth on the upstream and downstream sides of a dendrite arm growing at an angle with respect to the flow can be explained by the differences in the mean shapes of the two sides of the arm.

Results are also presented for free dendritic growth coupled with fluid flow for a pure material in three dimensions. They illustrate the strong influence of convection on the dendrite growth morphology. The knowledge of the flow and temperature fields in the melt from the simulations allows for a detailed understanding of the convection effects on dendritic growth in experiments.

**Keywords: dendritic growth, phase-field method, convection, flight**

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# **NUMERICAL AND EXPERIMENTAL INVESTIGATION OF THE SOLIDIFICATION OF A BOTTOM CHILLED CAVITY**

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The solidification of a bottom-chilled cavity filled with ammonium chloride is investigated in this work. The velocity field near the mushy region is measured and compared to computed results to improve on porosity models. This investigation also attempts to determine the suitability of two novel techniques, one experimental and one numerical, for studying solidification processes. A finite element/fictitious domain method is implemented to evaluate the performance of this approach for solidification problems. Experimental investigations to measure the velocity fields at various instants are carried out using Molecular Tagging Velocimetry (MTV).

The fictitious domain method is well suited for rapid design since it eliminates the need for a boundary conforming mesh. In this technique, the domain of the original problem is extended to a larger and simpler auxiliary domain with periodic boundary conditions. Lagrange multipliers are then used to enforce the original boundary conditions. This approach gives rise to efficient numerical scheme, but increases the memory requirements. Simple problems are solved to illustrate the methodology.

The MTV method was used to measure the velocity field directly above the chimneys and the adjacent mushy zone. Efforts are currently underway to measure both temperature (using laser induced fluorescence or LIF) and velocity fields simultaneously, as well as reducing the cavity size. The use of MTV/LIF will provide novel experimental results spanning various cavity sizes and chilled configurations. This will demonstrate the capabilities of the MTV/LIF method, provide verification of the modeling approaches proposed, and provide benchmark velocity and temperature field data valuable to other analytical and numerical studies, as well as enhance our understanding of thermo-solutal convection processes. Efforts to obtain micro-scale field measurements around the mushy zone are currently under way.

**Keywords: molecular tagging velocimetry, finite elements, fictitious domain**

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**KINETIC EVOLUTION OF STABLE AND METASTABLE STATES  
IN PROTEIN SOLUTIONS**

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We have experimentally and theoretically investigated the crystallization and metastable liquid-liquid phase separation in the  $\gamma$  crystallins, a family of eye-lens proteins. Specifically, we have used bovine  $\gamma$ -B crystallin as a model system to study the role of the individual cysteine residues in the phase separation of the  $\gamma$  crystallins. We compared the thermodynamic and kinetic behavior of recombinant wild type protein and the Cys 18 to Ser mutant. We found that the two proteins display essentially identical phase boundaries. The kinetics of crystallization, however, are very different. Despite this difference, the two proteins were found to have the same crystal forms and almost identical x-ray structures. Our results demonstrate that even conservative point mutations can bring about dramatic changes in the kinetics of crystallization.

We also have investigated the role of small polymers in determining the location of phase boundaries and the kinetics of the phase transformations. Our research is motivated by the extensive practical use of polyethylene glycol (PEG) as a precipitating agent in protein crystallization and liquid-liquid phase separation. Currently, there is no satisfactory description of the mechanism by which PEG induces phase separation in protein systems. In order to understand the precipitating action of PEG, we have used bovine  $\gamma$ -D crystallin as a model system to study the effect of low molecular weight (200 to 3350Da) PEG on the protein liquid-liquid phase transition. Liquid-liquid phase separation is not only a powerful tool for the analysis of protein-PEG interactions, but the role of the liquid-liquid phase boundaries itself is believed to be relevant to the protein crystallization kinetics. The aqueous  $\gamma$ -D crystallin system displays a liquid-liquid coexistence curve with an upper consolute critical temperature of 278K. Measurements of phase separation temperatures as a function of both protein and PEG concentration were determined for several PEG molecular weights. In addition, both PEG and protein concentrations in the coexisting phases were also obtained. The results show that PEG produces an increase of the critical temperature, while leaving the protein critical concentration unchanged. The critical temperature increases with both PEG concentration and molecular weight. A strong correlation between PEG repartitioning in the coexisting phases, and an increase in the cloud temperatures was also observed. We shall interpret our experimental results using depletion force theories well established for colloidal systems. Our work shows that PEG is a promising tool for inducing liquid-liquid phase transitions of protein aqueous systems.

**Keywords: crystallization, liquid-liquid phase separation, PEG,  $\gamma$  crystallin, kinetics, theoretical**

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# NANOTUBE-BASED STRUCTURES FOR SUPERSTRONG MATERIALS, NANOSCALE SENSORS AND DEVICES, AND EFFICIENT ELECTRON EMITTERS

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Carbon nanotubes are one of the most interesting new materials to emerge in the past decade, due to their outstanding mechanical and electrical properties. We have predicted, through large-scale *ab initio* simulations, that they are both incredibly elastic and the strongest materials known. These results have already been confirmed experimentally. However, our most recent calculations, which investigated the atomic transformations leading to fracture, found that the ultimate strength of atomically perfect nanotubes is substantially greater than the one observed experimentally, because these transformations are hindered by very large barriers. Due to their strength, low specific weight, and unusual electronic properties, nanotube-based materials will enable a variety of unique space and terrestrial applications: in superstrong fibers and composites, as strain and molecular sensors, in novel field emitters, and ultimately in nanoscale electronic devices.

Our most recent investigations focus on battery applications, pyro- and piezo-electric nanotubes, and nanotube-cluster assemblies for chemical sensors. Our dynamical simulations of Li diffusion show that Li ions are highly mobile inside carbon nanotube ropes and do not exhibit correlated motion even at fairly high concentrations, indicating the suitability of nanotube/Li materials for very high capacity batteries. Turning to pyro-electric effects, we have shown that most BN nanotubes exhibit a large, built-in electric field along the nanotube axis, as well as large piezoelectric coefficients. Our results show that BN nanotubes will be excellent components of nanotube-based nano-electro-mechanical systems (NEMS), including actuators, switches, and transducers. The spontaneous electric field also induces interesting effects in BN/C structures, where significant lowering of the work function can be accomplished by a suitable arrangement of BN/C junctions, leading to substantially enhanced electron emission. Turning to nanotube-cluster systems, we have shown that carbon nanotube-metal-cluster assemblies behave as effective chemical sensors. Using an Al cluster attached to a metallic nanotube, an effective semiconducting nanowire was created, whose electrical response changes dramatically upon adsorption of ammonia onto the metal cluster. Our *ab initio* results explain the observed behavior in terms of interactions between the molecular species and the nanotube-cluster system, where successive charge transfers between the components tailor the electronic and transport properties.

**Keywords:** nanotubes, superstrong materials, nanodevices, sensors, field emitters, nanostructures

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**DISPERSION MICROSTRUCTURE AND RHEOLOGY IN CERAMICS PROCESSING**

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Ceramics provide a potentially very useful class of materials owing to their physical properties; they are light, hard, resistant to abrasion, chemically inert, stable at high temperatures, and excellent thermal and electrical insulators. Further, by casting from a liquid suspension and subsequently sintering, many complex parts and shapes can be fabricated. Although the resultant properties of ceramics can be outstanding, they often suffer from extreme brittleness, caused by the propagation of cracks, which is in turn due to microstructural defects. These defects may be caused by a number of different factors, such as particle agglomeration, migration or segregation prior to sintering, or due to inhomogeneous volume change upon sintering.

Typically, high-performance ceramics are produced using monodisperse micron-sized particulate suspensions from which the ceramics are cast. By controlling the size and processing, a dense uniform microstructure may be formed prior to sintering. This route has met with limited success even though the maximum volume fraction of ceramic particulates that can be achieved prior to sintering is 0.74. The limited success may stem from the fact that a perfect crystal of mono-sized particles has slip planes that yield easily, and from the fact that there is still a large amount of void space that must be eliminated upon sintering.

An alternate approach is to use a mixture of particle sizes. It is well known that solids fractions of 90% can be obtained with a bidisperse suspension of spherical particles. Crystalline slip planes can be eliminated with a mixture of particle sizes. In addition to achieving high solids fractions, and therefore reducing potential sintering inhomogeneities, a mixture of two different types of particles can also impart desirable properties in a 'composite' ceramic. Owing to size or compositional differences, particle mixtures are subject to gravitational phase separation or demixing, which can severely limit the utility of these systems. Thus, processing in microgravity may provide an attractive environment for producing advanced ceramics.

We have developed a new  $O(N \ln N)$  simulation method with full hydrodynamics – Accelerated Stokesian Dynamics – to study the microstructure and determine the macroscopic properties of colloidal dispersions used in ceramics processing. Results are obtained for the shear and normal stresses, particle diffusivities and the shear-induced microstructure.

**Keywords: ceramics, Stokesian Dynamics, computer simulation, new research**

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# OPTICAL ELLIPSOMETRY AND X-RAY SCATTERING FOR CHARACTERIZING ORDER IN LIQUID CRYSTALLINE POLYMERS AND BIOPOLYMERS

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We report results of optical and wide and small angle X-ray scattering studies of structure development in collagen-model peptides. Our custom built two-dimensional optical ellipsometer is used to provide retardance and azimuthal angle information about the state of order in optically anisotropic structures. Recently, we have applied this instrumentation to investigate biological molecules, viz., oligomeric peptides with amino acid structures that are models for collagen. Proline and hydroxyproline residues stabilize the triple-helical conformation of collagen proteins in the collagen consensus sequence. Regular modifications have been introduced into the collagen consensus sequence, forming model systems for the study of bio-macromolecular organization. The model systems are oligomers with hexapeptide sequences of the form: (Glu) (Gly-Ala-Pro-Gly-Pro-Pro) (Glu) or (Glu) (Gly-Pro-Ala-Gly-Pro-Pro) (Glu). The glutamic acid capping the ends of the hexapeptide sequences imparts solubility in water. Depending upon concentration and temperature, the peptides form lyotropic liquid crystalline structures, and maintain their order when dried to powders suitable for X-ray studies. Through the use of the high intensity source of X-radiation at the Brookhaven National Synchrotron light Source, phase transformation kinetics and structure development are studied *in-situ*, providing time-resolved characterization of these peptides. Coupled with the optical imaging ellipsometry, these approaches provide the most complete information about microstructure in these systems. The goal of our research is to evaluate the ability of these model peptides for self-assembly into liquid crystalline and true three-dimensional crystalline phases and to assess the temperature stability of resultant higher order structures.

**Keywords: optical ellipsometry, x-ray scattering, liquid crystals, polymers, biopolymers**

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## **STEP BUNCH EVOLUTION ON VICINAL FACES OF KDP**

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For in-situ studies of the formation and evolution of step patterns in solution growth, we have assembled an experimental setup based on Michelson interferometry with the growing crystal surface as one of the reflective surfaces. The device allows data collection over a relatively large area (approximately 4 sq. mm) in situ and in real time during growth. The depth resolution is improved over traditional interferometry using phase-shifted images combining by a suitable algorithm. We achieve a depth resolution of approximately 50 Angstroms. Lateral resolution, dependent on the degree of magnification, is around 0.3 to 5 microns.

The crystal chosen as a model in this work is potassium dihydrogen phosphate (KDP), the optically non-linear material widely used in frequency doubling applications. Kinetics of KDP crystallization is well studied so that KDP can serve as a benchmark for our investigations. We present quantitative results on the onset, initial stages and development of instabilities in moving step trains on vicinal crystal surfaces at varying supersaturation, flow rate, and flow direction. The kinetics data suggest that at low supersaturations, step bunching is caused by impurity retardation of the steps, while at higher supersaturations, we link the non-linearity during growth to interdependence of the velocity and density of the steps evidenced in independent experiments. The behavior on the surface is very dynamic, small bunches both merge and split from larger bunches as they travel across the facet. We present evidence that despite these dynamics, under steady conditions there exists a limiting value to step bunch height. This height is reached at distances between 600 and 1000  $\mu\text{m}$  from the step source. In our experiments, we observed the retention of this step bunch height limit up to the path of 1500  $\mu\text{m}$ .

**Keywords: solution growth, stability, steps, KDP, interferometry**

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## FORCES DURING MANUFACTURE AND ASSEMBLY OF MICROSCALE DISCRETE ELECTRONIC COMPONENTS

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The manipulation of micron scale components in both fluid and air using AC and DC electric fields was explored. An apparatus for manipulating micron-scale dry dielectric materials has been developed. This method is expected to be applicable for transfer of a wide range of dielectric powders as well as small, shaped components. High throughput materials development could be extended through this method to areas such as the formulation of phosphors, pigments, brake pads, and adhesives. Small, 150  $\mu\text{m}$  diameter silica spheres, sodium fluorescein powder, and 100 nm polystyrene spheres have been dispensed with this apparatus. The dielectrophoretic force used to manipulate the particles may be controlled by selecting the appropriate electrode geometry and by adjusting the electric field intensity. This determines the amount of powder collected at the electrodes. As little as 1.0  $\mu\text{g}$  of sodium fluorescein powder, and as much as 16 mg of silica beads have been collected using this technique, and repeatability within 10 % of the total amount dispensed has been achieved. A similar electric field technique has been used to manipulate micron scale silica particles in an aqueous medium. Metal microelectrodes were prepared by lithographic patterning. Particle motion was imaged in real time using an inverted metallurgical microscope focused on the plane containing the particles. Particles were observed to pack at the electrodes in the presence of an applied DC field. This particle motion was characterized as a function of field strength, pH, and ionic strength of the background electrolyte. AC fields were also employed in an attempt to reduce the polarization of the particles and electrodes. A novel particle chaining process is reported during which particles aggregate in single lines parallel to the applied AC field. This motion was imaged using strobe photography in an attempt to isolate the effects of viscous drag on the assembly of the particles. Particles were also seen to adhere to the sapphire substrate near the electrodes during application of the field. A technique for tracking the two dimensional stochastic motion of particles settled on the substrate was developed and used to characterize the adhesion as a function of pH and ionic strength. Electrokinetic measurements for the particles and substrate were used as inputs to a dissimilar surface charge interaction model. The potential energy was calculated and used to explain the observed adhesion.

**Keywords:** electrophoretic forces, electrophoresis forces, high-throughput development, component assembly, particle motion, new research

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## **MODELING DENDRITIC GROWTH WITH FLUID FLOW IN THREE DIMENSIONS**

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Dendritic growth is important because it is the canonical form of crystallization in metallic systems. The microstructure formed during solidification determines the material properties of the product in service. NASA has had a sustained and successful effort in the study of dendritic growth, and this work supports the experimental investigations through advanced computation.

Pattern selection during dendritic growth is understood to be the result of the interaction of crystalline anisotropy and transport in the liquid and solid phases. In the absence of fluid flow, the transport is controlled by diffusion. However, the transport in these systems can be strongly affected by the presence of fluid flow during solidification. Advection of energy and solute dominate diffusion, and this provides an opportunity to modify and control the microstructure.

In this work, we use the phase-field method to simulate dendritic growth with fluid flow. The transport process in such a system is inherently three-dimensional. The phase-field method has become the method of choice for simulating dendritic growth, because it permits the representation of complex microstructures, as well as a natural way to handle coarsening and coalescence, both of which are important parts of the microstructural evolution. The method requires very fine resolution, and thus we are faced with a difficult computational problem. We have developed an adaptive finite element method approach that permits us to handle the large-scale three-dimensional problems posed. The code is implemented in parallel, so that computations can be performed in realistic times.

We demonstrate the fidelity of the code on known problems first. We then consider numerous problems for which experimental data is available. Our computations show that some experiments are contaminated by wall effects, even at very low flow rates and undercooling. We demonstrate the mechanisms for structure modification, and examine the theory of dendrite growth under the influence of flow.

**Keywords: dendrites, 3-D, phase-field, parallel computing**

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# KINETICS OF NUCLEATION AND CRYSTAL GROWTH IN GLASS FORMING MELTS IN MICROGRAVITY (NASA GRANT #NAG8-1465)

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The objective of this flight definition program is to obtain the first experimental data for the nucleation rate ( $I$ ), crystal growth rate ( $U$ ), and concentration of quenched-in nuclei ( $N_q$ ) for a well characterized silicate melt (lithium disilicate,  $LS_2$ ) processed entirely in space (low gravity). These low-g values will be compared with the  $I$ ,  $U$ , and  $N_q$  values for the same glass composition prepared identically on earth (1g). Although unexplained by the current theories for the kinetics of nucleation and crystal growth, there is significant experimental evidence suggesting that the values for  $I$ ,  $U$ , and  $N_q$  for a low-g glass should be smaller than those for a comparable glass on earth. No data are currently available for directly comparing these parameters for a low-g and a 1-g glass. The results from the proposed flight experiments are expected to advance our current scientific understanding of the nucleation and crystal growth kinetics in glasses, and to improve the technology currently used to manufacture inorganic glasses, glass-ceramics, and bulk metallic glasses.

The exact reason why a space glass is expected to have smaller values for  $I$ ,  $U$ , and  $N_q$  than an identical glass prepared on earth is unknown at this time, but a phenomenon based on “shear thinning” is considered a likely explanation. Shear thinning is the reduction in viscosity, which occurs with increasing shear rate in non-Newtonian liquids at a constant temperature. We believe that the gravity-driven convection that occurs in a melt on earth produces a higher shear rate than will occur in a nearly stagnant (convection-free) melt in space. Thus, the viscosity of a melt in low-g (space) could be higher than the viscosity of the same melt on earth. A higher viscosity (less shear thinning) for the space glass should result in smaller values for  $I$ ,  $U$ , and  $N_q$  than those for a similar glass on earth.

Ground-based experiments to verify the shear thinning hypothesis have been performed by heating bent  $LS_2$  glass fibers at temperatures (370 to 400° C) well below the temperatures for nucleation (425 to 500° C) and crystal growth (> 570° C). The glass fibers are bent in such a way that the bent portion contains varying amounts of flexural stress. The bent regions of the glass fibers, which were under stress (where shear thinning would occur) showed a higher nucleation and crystal growth than the unstressed parts of the fiber (no shear thinning), which is consistent with the concept of shear thinning (lower viscosity at bent portion). Our results from the ground-based experiments, which demonstrate that a flexural stress can enhance the nucleation and crystal growth in glasses, are described and discussed in this paper. The experimental protocol for our flight experiments is also presented and discussed.

**Keywords:** glass, nucleation and crystal growth rates, shear thinning, low gravity, flight

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## RECOVERY OF MINERALS IN MARTIAN SOILS VIA SUPERCRITICAL FLUID EXTRACTION

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We are using supercritical fluids to extract mineral from Martian surface soils and its igneous crust. Supercritical carbon dioxide will be used as the solvent. The Martian atmosphere is composed mostly of carbon dioxide (~95.3%) and could therefore provide an in-situ source of carbon dioxide as a supercritical solvent. We are conducting screening studies to determine which inorganic compounds are soluble in supercritical carbon dioxide. We are focusing on compounds which are hydrated in an attempt to recover both the water of hydration and to determine if the compounds are soluble in supercritical carbon dioxide. Once we have determined a substance is soluble, then we will perform a complete solubility study as a function of pressure and temperature. We have examined the following hydrated compounds: cupric nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ), nickel nitrate  $\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$ , zinc sulfate  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , sodium borate  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , ferric ammonium sulfate  $\text{Fe}(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , manganous sulfate  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ , ferric chloride  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and cupric sulfate  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Except for sodium borate which showed no water recovery, water recoveries have varied between 7% for cupric sulfate down to 0.1% for cupric nitrate of total sample weight. Water is soluble up to a mole fraction of 0.05 in supercritical carbon dioxide at a pressure of 350 bar and 304 K. In addition to the equation of state methods to predict solubility, we are trying to predict the solubility using molecular simulation. In molecular simulations, e.g., Monte Carlo simulation and Molecular Dynamics, the thermodynamic properties of a fluid are determined from information on the pair potential between encountered molecules. This effort is a collaboration with Professor Gerd Maurer from the Universitaet Kaiserslautern in Germany. He has performed simulations, which show the solubility of water in supercritical carbon dioxide to be 0.025 mole fraction at 110 C and 100 bar. Data collected by other investigator and our own data show the solubility to be higher, approximately 0.052 mole fraction. The equation of state method predicts a solubility of about 0.1 mole fraction. Another possible path to water would be through the reactions of supercritical carbon dioxide with species such as Talc, Tremolite (Amphibole), or Chrysotile (Serpentine). These more complex crystal structures are more likely to trap the hydrogen molecules. Water can be released by reaction with supercritical carbon dioxide. We have obtained talc samples and are beginning experiments with talc and supercritical carbon dioxide.

**Keywords:** water on Mars, extracting minerals on Mars, supercritical extraction, ISRU

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# MODELING THREE-DIMENSIONAL FLOWS AND G-JITTER DURING MICROGRAVITY BRIDGMAN GROWTH

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Buoyancy-driven melt convection dominates mass transport in many crystal growth systems, thereby having a critical effect on solute segregation. Since segregation in turn plays a key role in determining the properties of grown materials, there is widespread interest in the application of various methods to modify or suppress convection. In this vein, microgravity crystal growth promises great benefits for better understanding and control of buoyant flow. However, even small changes in acceleration (i.e., g-jitter) can drive flows significant enough to affect segregation.

We present an overview of a new finite element model for the parallel computation of three-dimensional flows, segregation, and solidification during Bridgman crystal growth. The model features a self-consistent coupling between the field phenomena (fluid flow, heat and mass transfer) and interfacial effects (solidification) via front-tracking techniques. Also of note is a new coupling with a sophisticated furnace model, the CrysVUN++ code of Mueller et al., to provide realistic heat transfer boundary conditions.

We present initial results for several three-dimensional systems, including an ground-based horizontal Bridgman system and a prototype system for microgravity and g-jitter.

**Keywords:** 3-D modeling, segregation, g-jitter, convection, finite element method, theoretical

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**FIRST PRINCIPLES CALCULATIONS OF LIQUID II-VI COMPOUNDS AT  
TEMPERATURES ABOVE AND BELOW THEIR MELTING POINTS**

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This presentation will highlight results obtained from quantum mechanical molecular dynamics simulations of the liquid state of several II-VI tellurium-containing compounds, notably CdTe and ZnTe. These materials are employed in a variety of technologically important electronic and electro-optical devices; however, their growth has typically proven to be extremely difficult. We seek to obtain a more fundamental understanding of the properties of these compounds so that the physical mechanisms responsible for growth can be elucidated.

Our simulations use the pseudopotential density functional method (PDFM) to calculate quantum forces in the melt. We prepare a liquid state ensemble using supercells and Langevin dynamics to thermalize the liquid. One of the most interesting issues in these materials concerns the conductivity of the liquid state. Most Group IV and III-VI semiconductors are metallic in the liquid state; however, some II-VI semiconductors remain semiconducting in the melt. In order to examine this problem in more detail, we have calculated the conductivity of a prototypical III-V semiconductor (GaAs) and compared its properties to II-VI semiconductors. Our demonstration illustrates the microstructure of the liquid state and the self-diffusion of different species within the melt. We will also discuss why it may be difficult to grow Te-containing II-VI's from the melt.

**Keywords:** II-VI compounds, atomistic computations, molecular dynamics, pseudopotentials, theoretical

# REAL-TIME OPTICAL MONITORING AND SIMULATIONS OF GAS PHASE KINETICS IN InN VAPOR PHASE EPITAXY AT HIGH PRESSURE

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Understanding the kinetics of nucleation and coalescence of heteroepitaxial thin films is a crucial step in controlling a chemical vapor deposition process, since it defines the perfection of the heteroepitaxial film both in terms of extended defect formation and chemical integrity of the interface. The initial nucleation process also defines the film quality during the later stages of film growth. The growth of emerging materials heterostructures such as InN or indium-rich  $\text{Ga}_x\text{In}_{1-x}\text{N}$  requires deposition methods operating at high vapor densities due to the high thermal decomposition pressure in these materials. High nitrogen pressure has been demonstrated to suppress thermal decomposition of InN, but has not been applied yet in chemical vapor deposition or etching experiments. Because of the difficulty with maintaining stoichiometry at elevated temperature, current knowledge regarding thermodynamic data for InN, e.g., its melting point, temperature-dependent heat capacity, heat and entropy of formation have to be established with high accuracy. Also, no information exists regarding the partial pressures of nitrogen and phosphorus along the liquidus surfaces of mixed-anion alloys of InN. The extension of chemical vapor deposition (CVD) to elevated pressure is also necessary for retaining stoichiometric single phase surface composition for materials that are characterized by large thermal decomposition pressures at optimum processing temperatures.

The here presented research focuses on the base material InN and addresses both: the prediction and simulation of gas phase reactions and surface kinetics of InN growth at high pressures, and the real-time optical monitoring of gas phase- and surface chemistry processes during high pressure CVD of InN. For the experimental validation, we constructed a high pressure CVD reactor with integrated optical diagnostics to monitor in real-time gas flow dynamics, gas-phase decomposition kinetics, and the film growth process itself. These experimental data are of crucial importance to provide (a) input parameter for process models and simulation codes, and (b) establish growth parameter sets needed for analysis and control of chemical vapor deposition at elevated pressure. Access to microgravity is required to retain high pressure conditions of laminar flow, which is essential for successful acquisition and interpretation of the optical data. We describe the present status of our modeling and simulations efforts on gas phase and surface reactions kinetics for InN growth at high pressures, which is based on a numerical solution of nonlinear, coupled partial differential equations representing the conservation of momentum, energy and total mass as well as balances over the individual species involved in the InN deposition. We also describe the implementation of the high pressure CVD reactor system and the optical methods of real-time process monitoring to analyze the initial stages of heteroepitaxy and steady-state growth in the different pressure ranges.

**Keywords:** real-time monitoring, high-pressure CVD, gas phase kinetics, thin film epitaxy, new research

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**HIGH TEMPERATURE PHASES AND PHASE EQUILIBRIA IN REACTIVE  
MOLTEN METAL-BASED SYSTEMS**

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Currently, the information on high-temperature/low-pressure phase equilibria is scarce for metal-oxide-gas systems where components have high chemical reactivities at elevated temperatures and formed phases are characterized by greatly different melting points. Examples include Al-O-H, Mg-O, Zr-O-N, Ti-C-O-N, B-C-O, etc. Our goal is to investigate stable and metastable phase relations in such systems at temperatures above 2000 °C. This information will be valuable for both fundamental understanding of the nature of these materials and for their practical use in many areas including high energy density additives to propellants and explosives, gas sensors, fuel cells, and ultra-hard coatings.

The use of microgravity will enable us to set up a containerless experiment in which the sample can be preheated to and maintained at a constant temperature without gravitational phase separation due to the density difference. Current efforts have been focused on the design of the experimental setup. A 20 kHz ultrasonic levitator has been designed and built for sample positioning and a 125 W CO<sub>2</sub> laser is used for sample heating. The sample is positioned and heated in a controlled environment chamber with transparent Lexan walls. The laser radiation is delivered to the sample via an enclosed beam-guiding and focusing system; both incident and reflected laser beams are used to heat the sample simultaneously from two opposite sides to minimize the temperature gradients. In-situ diagnostics include a three-wavelength pyrometer coupled to a PC-based data acquisition system and a video camera enabling one to monitor the sample's temperature and position, respectively. Samples used in the experiments are pressed powder pellets (~ 2 mm diameter) with specific bulk compositions. During the planned microgravity experiments, the pellet will be positioned using the levitator, heated to a constant temperature using the laser beam, and then rapidly quenched between two colliding brass plates. Quenched samples will be analyzed for phase make-up, structure and composition with quantitative TEM and SEM. Provisions to sample and analyze the post-experiment atmosphere are currently being made. The microgravity experiment will be conducted onboard of a KC-35 aircraft flying parabolic trajectories. Presently, the design and set-up of the experimental apparatus have been completed and initial normal gravity tests are in progress aimed to identify the laser power required, and determine the details of the timing and control of the microgravity tests.

**Keywords: containerless experiments, levitator, metal-oxide, metal-gas, phase equilibria, new research**

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# THE EFFECT OF SIMULATED MICROGRAVITY ON SURFACE REACTIONS AND ADSORPTION OF SERUM PROTEINS ON BONE-BIOACTIVE MICROCARRIERS

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Biomimetically modified bioactive materials with bone-like surface properties are attractive candidate for use as microcarriers for 3-D bone-like tissue engineering under simulated microgravity conditions of rotating wall vessel (RWV) bioreactors. The biomimetic surface modification includes formation of bone-like minerals at the surface and adsorption of serum proteins critical for bone cell attachment and function. Previously, we reported a major effect of simulated microgravity on chemical reactions of bioactive glass (BG) in physiological solutions. Reaction kinetics and subsequent formation of Ca-P phases at the BG surface were significantly enhanced. In this paper, we document the effects of simulated microgravity on the adsorption of serum proteins onto BG as a microcarrier material.

BG 45S5 granules were used for the study. A High Aspect Ratio Vessel (HARV-50 ml, Synthecon, Houston, TX) was used to simulate microgravity conditions. As reported before, a rotational speed of 10 rpm and a particle size range of 40-70  $\mu\text{m}$  were chosen to ensure simulated microgravity conditions for the BG particles. Control unit gravity experiments were conducted under static conditions. BG particles used were either unconditioned (BG-UN) or conditioned. When conditioned, either an amorphous calcium phosphate (BG-ACP) or a carbonated hydroxyapatite (BG-cHA) was formed at the BG surface. For adsorption of serum proteins, BG particles were immersed in MEM complemented with 10% newborn bovine serum for 2 hours. The concentration of extracted serum proteins was measured using Bio-Rad detergent compatible (DC) assay and colorimetry.

It was found that the amount of proteins adsorbed onto BG-UN microcarriers under static conditions was 10 times larger than that reported for porous BG discs. In comparison to BG-UN, the amount of proteins adsorbed to BG-ACP and BG-cHA particles increased more than two and three times, respectively. Further increase in these amounts was observed under simulated microgravity conditions: the amount adsorbed onto both unconditioned and conditioned BG doubled (a 100% increase). The effects of ACP and c-HA phases on protein adsorption on BG are in agreement with previous reports. The effect of simulated microgravity can be interpreted using our numerical analysis: the lack of sedimentation, very low shear stress, and the dual mechanisms of mass transport – diffusion and convection – are likely to be at the basis of the enhanced protein adsorption in the HARV. The present experiments also reveal the role of interfacial mass transfer on protein adsorption.

This study demonstrates the major effects of a large surface area, surface conditioning, and simulated microgravity on adsorption of serum proteins onto BG microcarriers. In this regard, this data in combination with our previous reports on the effects of simulated microgravity on the BG surface transformations, suggest that the surface reactions critical for a substrate for 3D bone tissue engineering are enhanced in RWV bioreactors simulating microgravity conditions.

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**Keywords: simulated microgravity, microcarriers, protein adsorption, surface reactions, 3D tissue engineering, biomaterials**

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## FUNDAMENTAL STUDIES OF CRYSTAL GROWTH OF MICROPOROUS MATERIALS

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Microporous materials form an important class of solids with diverse technological applications in chemical, petrochemical and consumer industries. These materials are characterized by pores, cages and channels of molecular dimensions ( $<15$  Å) and are the sites for adsorption, hydrocarbon transformations and ion-exchange.

The goal of our NASA program is to develop a better understanding of the crystallization process, which should facilitate directed synthesis of new morphologies and materials. We have taken a four-pronged strategy for our ground-based studies, primarily dealing with zincophosphates and aluminosilicate zeolites.

Using reverse micelles (RM), which are nanometer-sized droplets of aqueous solutions in a hydrocarbon (oil) medium, we have demonstrated that considerable control can be exercised over topology, morphology and crystallization pathways as compared to conventional hydrothermal synthesis (HS) methods. In collaboration with Prof. M. George at the University of Alabama, Huntsville, we have shown that RM crystals have atomically smooth single layer surfaces, considerably smoother than the best space grown microporous samples. Our hypothesis is that the water layer around the crystal in the RM method modulates the types of molecular species, thereby providing controlled attachment kinetics.

Dr. N. Ramachandran of MSFC has developed algorithms for modeling microporous crystal growth using population balance models. This program is currently being used to contrast the early nucleation events in hydrothermal synthesis of zincophosphates using two different structure directing agents. Information regarding the types of nucleation species should be forthcoming from these studies.

We have recently completed a study comparing the dissolution of two microporous zincophosphate structures. Even though we could not determine the molecular structure of the dissolving units, by use of an in situ spectroscopic method, we concluded that the size of the primary dissolution unit of the two topologies was distinct. We are working on the hypothesis that both attachment units and dissolution units of different frameworks are different.

Since nanometer-sized seeds were found to be effective in growing crystals in the RM system, we are extending this seeding concept to aluminosilicate zeolites, in collaboration with Dr. Brian Schoeman of Dow Chemical Co. We are using as seeds nanosized particles recovered from a typical clear solution synthesis. Using these seeds, we have synthesized zeolites A, Y and sodalite from identical nutrient solutions, demonstrating the effect of seeds as the controlling feature in the crystallization. Previous studies have focused on macroscopic seeds, our contribution has been to show that memory of crystals is retained even in nanometer-sized particles.

Our eventual plan is to use microgravity environment to verify that crystal growth/dissolution of frameworks with distinct morphologies occur via molecular units differing in size and composition. By measuring rates of growth/dissolution in microgravity and 1g, and exploiting the influence of convection on the processes, we intend to obtain information on the size of the attachment/detachment species with the help of crystal growth models.

**Keywords:** zeolite, reverse micelle, modeling, nanoparticles, AFM

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# METALLIC AND INTERMETALLIC NANOPARTICLE FILAMENTS AND TREE-LIKE ASSEMBLIES PREPARED BY LASER VAPORIZATION CONTROLLED CONDENSATION

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Nanoparticles exhibit interesting properties that are usually different from the bulk materials' properties. The evolution of the nanoscale properties is largely dependent on the size, shape and assembly of the nanoparticles. The general objective of the ground-based experiments is to advance the scientific understanding of nucleation and materials synthesis from the vapor phase, which are strongly influenced by gravity and convection effects. In this work, we present a method to synthesize size-selected nanoparticles of a variety of materials by coupling the laser vaporization controlled condensation (LVCC) technique with a differential mobility analyzer (DMA). The LVCC method is based on using pulsed laser vaporization within well-defined conditions of temperature and pressure in a thermal diffusion cloud chamber. The coupling of LVCC and DMA is applied to synthesize Al, Fe, Ni, Ti and FeAl intermetallic nanoparticles of selected sizes.

The LVCC method can be coupled to plasma and ionic polymerization techniques, thus allowing the incorporation of the metallic nanoparticles within the polymer films. The size of the product polymer particles is limited in normal gravity by gravitational settling. The application of microgravity to the study of gas phase polymerization is expected to result in a better control of the process and may also lead to important technological advances. The effect of electrical charging of the nanoparticles by ions and free electrons generated by the laser vaporization process has been investigated. Enormous electrostatic aggregation due to dipole forces is observed between nanoparticles to form chain aggregates, and between the chain aggregates to form tree-like filaments. The tree-like aggregates may have special applications as fillers or additives to increase the elastic modulus and tensile strength of polymers such as low strength rubbers. These materials could have unique properties and may lead to new practical and technological applications.

**Keywords:** nanoparticles, intermetallic, polymer, filaments, tree-like

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## **MECHANISMS FOR THE CRYSTALLIZATION OF ZBLAN**

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The objective of this ground based study is to test the hypothesis that shear thinning (the non-Newtonian response of viscosity to shear rate) is a viable mechanism to explain the observation of enhanced glass formation in numerous low-g experiments. In 1-g, fluid motion results from buoyancy forces and surface tension driven convection. This fluid flow will introduce shear in undercooled liquids in 1-g. In low-g it is known that fluid flows are greatly reduced so that the shear rate in fluids can be extremely low. It is believed that some fluids may have weak structure in the absence of flow. Very small shear rates could cause this structure to collapse in response to shear resulting in shear thinning of the fluid. The hypothesis of this research is that:

Shear thinning in undercooled liquids decreases the viscosity, increasing the rate of nucleation and crystallization of glass forming melts. Shear in the melt can be reduced in low-g, thus enhancing undercooling and glass formation.

The viscosity of a model glass (lithium di-silicate, L2S) often used for crystallization studies has been measured at very low shear rates using a dynamic mechanical thermal analyzer. Our results are consistent with increasing viscosity at low shear rates. The viscosity of L2S may vary as much as an order of magnitude depending on the shear rate in the temperature region of maximum nucleation and crystal growth. Classical equations for nucleation and crystal growth rates, are inversely related to the viscosity and viscosity to the third power respectively. An order of magnitude variation in viscosity (with shear) at a given temperature would have dramatic effects on glass crystallization. Tests are beginning with the heavy metal fluoride glass ZBLAN ( $\text{ZrF}_2\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3\text{-NaF}$ ).

Crystallization studies with ZBLAN to examine the effect of shear on crystallization have begun. Samples are being melted and quenched under quiescent conditions and with controlled shear to determine the effect on crystallization.

The results from this study are expected to advance the current scientific understanding of glass formation in low-g and glass crystallization under glass molding conditions and will improve the scientific understanding of technological processes such as fiber pulling, bulk amorphous alloys, and glass fabrication processes.

**Keywords: shear thinning, glass, ZBLAN, glass formation, low gravity, new research**

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# INVESTIGATION OF THE CRYSTAL GROWTH OF DIELECTRIC MATERIALS BY THE BRIDGMAN TECHNIQUE USING VIBRATIONAL CONTROL

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Fluid convection is an important phenomenon in crystal-melt systems. When uncontrolled, it can lead to a variety of problems including the incorporation of defects into a growing crystal. In a microgravity environment, where solutal and thermal convection is minimal, g-jitter, random vibrations produced from various sources, has been found to cause undesirable fluid flow. One potential solution to this problem involves the introduction of precisely controlled convection to suppress these flows. Forced convection is already used in many earth-based crystal growth processes to improve crystal quality and growth rates by either inducing or suppressing the naturally occurring convection.

This research program has focused on convection induced through the application of low-frequency vibrations, either directly into the melt with a vibrating disk (applied vibrational control [AVC]), or external to the growth ampoule (coupled vibrational stirring). Both vibrational techniques produce significant convection, and the benefits/drawbacks of each technique will be discussed.

A water/glycerin system was used to determine important vibrational parameters and to make quantitative measurements of fluid flow produced through vibrations. Fluid flow was imaged with the aid of tracer particles. Important dependent variables such as fluid velocity profiles were measured as a function of vibrational settings, crucible geometry, and fluid properties.

The influence of vibrational flow was investigated in  $\text{NaNO}_3$ , a low temperature (306°C) growth system that could be directly observed with the aid of a transparent furnace. Effects on growth rate, interface shape and position, and doping profiles were observed. The effect of these techniques was also examined in high temperature systems (lead magnesium niobate-lead titanate for CVS and lead telluride for AVC).

**Keywords:** crystal growth, vibrations, fluid flow, convection, new research

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**FLIGHT PLANNING FOR THE INTERNATIONAL SPACE STATION -  
LEVITATION OBSERVATION OF DENDRITE EVOLUTION IN STEEL  
TERNARY ALLOY RAPID SOLIDIFICATION (LODESTARS)**

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During rapid solidification, a molten sample is cooled below its equilibrium solidification temperature to form a metastable liquid. Once nucleation is initiated, growth of the solid phase proceeds and can be seen as a sudden rise in temperature. The heat of fusion is rejected ahead of the growing dendrites into the undercooled liquid in a process known as recalescence.

Fe-Cr-Ni alloys may form several equilibrium phases and the hypoeutectic alloys, with compositions near the commercially important 316 stainless steel alloy, are observed to solidify by way of a two-step process known as double recalescence. During double recalescence, the first temperature rise is associated with formation of the metastable ferritic solid phase with subsequent conversion to the stable austenitic phase during the second temperature rise. Selection of which phase grows into the undercooled melt during primary solidification may be accomplished by choice of the appropriate nucleation trigger material or by control of the processing parameters during rapid solidification. Due to the highly reactive nature of the molten sample material and in order to avoid contamination of the undercooled melt, a containerless electromagnetic levitation (EML) processing technique is used.

During ground-based testing the weight of the sample pulls the molten droplet down into the magnetic field. This results in a variety of effects including accentuated inductive heating of the sample, increased convection, and sample deformation from its equilibrium spherical shape. In microgravity testing, convection may be controlled over a wide range of internal flows and the double recalescence behavior of Fe-Cr-Ni alloys is seen to change. This program is aimed at understanding how melt convection influences phase selection and the evolution of rapid solidification microstructures.

**Keywords: rapid solidification, recalescence, convection, flight**

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## GRAVITATIONAL EFFECTS ON DISTORTION IN SINTERING

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During sintering a powder compact gains strength through low-temperature interparticle bonding, usually induced by solid-state surface diffusion, followed by further strength contributions from high-temperature densification. In cases where a liquid phase forms, sintering densification is accelerated and shape retention is sustained while open pores remain and contribute capillary forces. Unfortunately, sintering densification requires the compact become thermally softened to a point where creep strain rates reach levels near  $10^{-2} \text{ s}^{-1}$  when the liquid forms. On the other hand, thermal softening of the powder compact substantially reduces the strength at high temperatures. Therefore, the *in situ* strength evolution during sintering is a primary focus to separate compact densification (as required for high performance) with minimized distortion (as required for net-shaping). With respect to gravitation effects on distortion during sintering there are two points of substantial weakness - prior to significant interparticle bonding and during final pore closure. This research is focused on understanding the competition among interparticle neck growth, densification, thermal softening, grain boundary wetting, capillary effects associated with liquid wetting and residual porosity, and gravity. Most surprising is the apparent role of gravity, where the deviatoric stress acting on the powder structure induces skeletal formation that reduces distortion. In contrast with theory, samples processed in microgravity have larger levels of distortion, yet fail to fully densify.

Results are presented on the experimental concepts supporting an emerging model of sintering strength evolution that enables understanding of both distortion and densification. The experiments have relied on tungsten heavy alloys, various combinations of dihedral angle, pore size, initial porosity, liquid:solid ratio, and heating rates. On Earth, the dominant factor with respect to distortion is the starting body heterogeneity. Current modeling efforts are seeking some means to uniformly predict the distortion based on a starting pore structure heterogeneity parameter. Densification is largely unaffected by the initial pore structure, but distortion is highly variable, suggesting that nonuniform pore closure might be a significant parameter during sintering. With respect to flight experiments, plans include removal of the solid body forces acting on the solid grains, allowing stabilization of the pore structure and examination of the buoyancy effects with regard to distortion. In microgravity there is the surprising result that compacts do not densify, yet distort – a factor that is contrary to all current sintering models.

**Keyword: flight**

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**USE OF COMPUTED TOMOGRAPHY FOR CHARACTERIZING MATERIALS GROWN  
TERRESTRIALLY AND IN MICROGRAVITY**

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Computed tomography (CT) using a radioisotope of cobalt can provide NASA Principal Investigators (PI) rapid information, non-destructively, about their samples. In particular, density values, which can readily, and best, be obtained from (near) monochromatic CT, such as <sup>60</sup>Co, provide local compositional data about bulk samples. In addition, the technique provides information about grain size in two-phase materials, and also the porosity level and its distribution within the sample for large grained samples. The existing CT facility at NASA's Kennedy Space Center (KSC) is ideally situated to furnish information rapidly and conveniently to PIs, particularly immediately before and after flight missions. Efforts have been made on improving the protocol for determining density chiefly by considering the effect of the two, close energy lines (1.17 and 1.35 MeV) of the cobalt source separately, rather than averaging their effect during scattering.

CT is particularly suited for examining thermal expansion in a safe, highly isothermal environment. A single zone heat pipe furnace has been fabricated and has been installed on the CT table at KSC. Expansion of a material can be determined from measurements of the change in length with temperature (via digital radiograms), or the cross section area or the density (via the CT sections). Results will be shown for pure lead up to 915°C. This is a test sample and will be followed by data on a lead-5.94% antimony sample which is close in composition to the proposed flight sample of Professor Poirier. These data are useful for two reasons: first they are essential input parameters the Principal Investigator needs for doing fluid flow calculations, and secondly, they are needed by the engineering staff to design for thermal expansion in the Sample Ampoule Cartridge Assemblies (SACA).

Examples of the measurement of composition in solid solution alloys will be shown, including a seed crystal of a silicon-germanium alloy to be used by Dr. Szofran to grow Ge-Si by Bridgman growth.

Finally, an iron-nickel meteorite with a large volume percentage of iron sulfide has been examined to evaluate the dendritic arrangement and coarsening in a sample "annealed" over hundreds of millions of years. The section examined is 180 x 83 mm in cross section and 700 mm long, and has grain (dendrite sections) sizes of several cm. Three-dimensional views of the two-phase structure will be shown.

**Keywords: flight samples, composition, density, 3-D coarsening, meteorites, characterization**

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## EVOLUTION OF LOCAL MICROSTRUCTURES: SPATIAL CORRELATIONS IN COARSENING CLUSTERS

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Diffusion-limited capillarity-driven coarsening of precipitates is an important and intensively studied phenomenon in materials science. Phase coarsening can occur among microstructural constituents ranging from the primary phases to widely dispersed precipitates. The wide range of volume fractions,  $V$ , encountered in phase coarsening processes makes it essential to have a fundamental theory, or model, of phase coarsening that treats the volume fraction as a global parameter of the microstructure. The classic coarsening theory developed by Todes, Lifshitz, Syozov, and Wagner (TLSW theory, often termed LSW theory) is limited to *infinitesimally* small volume fractions, so  $V = 0$ . This highly idealized model proved useful to explain experimentally observed scaling time dependency of the characteristic size of precipitates, but poorly approximates their distribution in radii. TLSW theory neglects all direct intra-particle interactions and, as a consequence, neither is capable of describing the volume fraction dependence of the coarsening rate, nor any spatial correlations that may develop in the size distribution. This work uses computer modeling and holographic imaging to compare coarsening rates in relatively high volume fraction and low volume fraction microstructures by observing “mixed-dimensional” droplets (hemispherical droplets fixed on a surface undergoing coarsening by two-dimensional diffusion) during ground-based investigations. The method involves filling a cell with a homogeneous parent phase, and cooling below the consolute temperature to the isopycnic temperature within the two-phase region of a monotectic system. Three-dimensional ground-based testing involves slowly rotating the two-phase isopycnic system to compensate for the minute density differences between the phases to minimize sedimentation during long-term coarsening in 1-g. The microgravity objective is to study via holography three-dimensional coarsening in finite, but large clusters of droplets containing different volume fractions located at the central area of the observation cell.

Determination of sizes and positions of the many droplets in the holographic images requires automation. We have developed software for automated data analysis, and demonstrated good agreement between re-generated maps and scaled photographs of the original holograms for mixed-dimensional coarsening. The next step in automated analysis is to determine sizes and positions of droplets in the central volume of the observation cell.

The results of these experiments have led to the development of a detailed science requirements document (SRD) containing science protocols for ELMS. A formal Science Concept Review (SCR) was presented on December 17, 2001, to NASA representatives and external peer examiners.

**Keywords:** 3-D/mixed-D coarsening, holography, volume fraction, Ostwald ripening, flight

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**RIDGE/IDGE: DENDRITIC GROWTH & MELTING EXPERIMENTS****A. Lupulescu<sup>1</sup>, M.E. Glicksman<sup>\*1</sup>, J. Frei<sup>1</sup>, M.B. Koss<sup>2</sup>, and J.C. LaCombe<sup>3</sup>**<sup>1</sup>Rensselaer Polytechnic Institute, Troy, NY, <sup>2</sup>College Of The Holy Cross, Worcester, MA, <sup>3</sup>University Of Nevada, Reno, NV

The Isothermal Dendritic Growth Experiment (IDGE) is a basic science experiment to provide terrestrial and microgravity data on the kinetics and morphology of dendritic solidification under heat conduction control. The IDGE flew three times aboard *Columbia* as a primary payload on the USMP-2, -3, and -4 missions. IDGE instruments provided CCD images (telemetered during the flights), NASA-processed 35-mm film negatives (postflight), and on USMP-4, near-real-time streaming of video data. IDGE data provide benchmark crystal growth speed as well as tip radii measured as functions of the melt supercooling. The RIDGE program, designed as a follow-on to an ongoing MRD flight program, allows ground-based data reduction, mining, and analysis to enhance further understanding of these flight experiments. Two major subjects constituted the RIDGE focus over the past year: PVA sidebranching characteristics, and PVA dendrites melting in microgravity environment. The sidebranch characteristics of pivalic acid dendrites grown under convection-free (cf) and diffuso-convective (dc) conditions were investigated for supercoolings over the range of 0.1K to 1.0K. Results indicate that the distance from the dendrite tip to the first detectable sidebranch and to the first detectable coarsening event normalized by the tip radius,  $R$ , are independent of the supercooling. The sidebranch spacing in the uniform region near the dendrite tip, and the spacing in the coarsening region, if normalized by  $R$ , does not appear to have a significant dependence on convection or supercooling. When the envelope enclosing all sidebranches from the tip to the end of the coarsening region was fitted to a power law as a function of distance from the tip, we found that the pre-exponential and exponential terms were significantly different for the convection-free and diffuso-convective results. We now report on the melting process of a PVA dendritic mushy zone, observed for the first time under convection-free conditions. Conduction-limited melting processes are of importance in orbital melting of materials, meteoritic genesis and nebular processes, and in mushy-zone evolution, and in fusion weld pools, the latter two examples of melting where gravity is present but the length scales for thermal buoyancy are restricted. Microgravity video data show that PVA dendrites melt into fragments that shrink at accelerating rates to extinction. The melting paths of individual fragments follow characteristic time dependences. The theoretical melting kinetics against which the experimental observations are compared is based on the conduction-limited quasi-static process of melting under shape-preserving conditions. Good agreement between quasi-static theory and experiment was found for the melting of a needle-shaped prolate spheroidal PVA crystal.

Supported by NASA Microgravity Research Division.

**Keywords: dendrite, supercooling, mushy zone, prolate spheroid, characterization**

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## MACROVOID DEFECT GROWTH DURING EVAPORATIVE CASTING OF POLYMERIC MEMBRANES

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Macrovoid (MV) formation is a significant problem in evaporatively cast polymeric membranes. MVs are large, elongated or teardrop-shaped pores (10–50  $\mu\text{m}$ ) that impair the structural integrity of the membranes. Although MVs have been extensively studied, there is no general agreement on the mechanisms governing MV growth. Recently, our research group has formulated the solutocapillary convection (SC) hypothesis, which contends that MV growth involves three principal forces: a Marangoni force generated by surface-tension gradients within the MV interface, a viscous drag force, and a gravitationally induced body force. Two sets of complimentary experiments were conducted to test the SC hypothesis.

In the first set, ground-based videomicroscopy flow-visualization (VMFV) was utilized to measure the flow velocities at the MV-casting solution interface and deep within the casting solution. The measurements were performed with casting solutions containing 10 wt% cellulose acetate (CA), 30 wt% H<sub>2</sub>O, 60 wt% acetone, and 200-ppm TiO<sub>2</sub> (20-nm particles for flow visualization), and the surface tension was controlled by surfactant addition.<sup>2</sup> Qualitatively, the experiments indicated that MV growth occurs in three distinct phases: (1) a very rapid initial growth period, (2) a much slower growth phase, and (3) absorption of selected MVs into the expanding demixed region. The presence of tracer particles inside the MVs suggests the presence of a convective flow, which transfers the particles from the bulk solution to the MV interior. Although the VMFV experiments did not distinguish any surfactant effect on the interfacial velocities, a statistically significant effect on the MV number density was observed.

In the second set of experiments, membranes were cast aboard a KC-135 aircraft under 0-g and 2-g conditions. Despite careful attention to the design and fabrication of the membrane casting apparatus (MCA), several unforeseen problems were encountered, the most significant of which was the contamination of the casting solution by the activated carbon particles used for solvent adsorption. Despite these difficulties, SEM analysis of uncontaminated membrane samples indicated that the MV morphology was strongly influenced by the solvent-nonsolvent ratio. However, dependence of MV size and number density on the magnitude of the buoyancy force could not be established since (in many cases) the MVs penetrated through the entire thickness of the cast membrane. Based upon the insights obtained from these experiments, a new MCA has been designed, which incorporates wider casting wells, deeper recesses for casting thicker membranes, and better isolation of the activated carbon. The new MCAs will be used in an upcoming KC-135 flight, and should enable us to evaluate quantitatively the validity of the SC hypothesis.

**Keywords:** biomaterials, polymeric membranes, membrane morphology, macrovoid growth, solutocapillary convection, buoyancy effects

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**TOWARD UNDERSTANDING PORE FORMATION AND MOBILITY DURING  
CONTROLLED DIRECTIONAL SOLIDIFICATION IN A MICROGRAVITY  
ENVIRONMENT INVESTIGATION (PFMI)**

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The generation and inclusion of detrimental porosity, e.g., “pipes” and “rattails” can occur during controlled directional solidification processing. The origin of these defects is generally attributed to gas evolution and entrapment during solidification of the melt. On Earth, owing to buoyancy, an initiated bubble can rapidly rise through the liquid melt and “pop” at the surface; this is obviously not ensured in a low gravity or microgravity environment. Clearly, porosity generation and inclusion is detrimental to conducting any meaningful solidification-science studies in microgravity. Thus it is essential that model experiments be conducted in microgravity, to understand the details of the generation and mobility of porosity, so that methods can be found to eliminate it. In hindsight, this is particularly relevant given the results of the previous directional solidification experiments conducted in Space.

The current International Space Station (ISS) Microgravity Science Glovebox (MSG) investigation addresses the central issue of porosity formation and mobility during controlled directional solidification processing in microgravity. The study will be done using a transparent metal-analogue material, succinonitrile (SCN) and succinonitrile-water “alloys”, so that direct observation and recording of pore generation and mobility can be made during the experiments. Succinonitrile is particularly well suited for the proposed investigation because it is transparent, it solidifies in a manner analogous to most metals, it has a convenient melting point, its material properties are well characterized and, it has been successfully used in previous microgravity experiments. The PFMI experiment will be launched on the UF-2, STS-111 flight.

Highlighting the porosity development problem in metal alloys during microgravity processing, the poster will describe: (i) the intent of the proposed experiments, (ii) the theoretical rationale behind using SCN as the study material for porosity generation and migration and, (iii) the experimental protocol for the investigation of the effects of the processing parameters. Photographs of the flight experimental hardware, and the novel sample ampoule, will be exhibited. The experimental apparatus will be described in detail and a summary of the scientific objectives will be presented.

**Keywords: ISS glovebox, succinonitrile, directional solidification, porosity, microgravity, flight**

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**INTERDIFFUSION IN PbO - SiO<sub>2</sub> MELTS: EFFECT OF FREE CONVECTION****Prabhat K. Gupta\* and Yirong He**

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Understanding the kinetics of a variety of technologically important processes such as crystal growth, homogenization, and phase separation requires accurate measurements of the interdiffusion coefficients. Accurate measurements of diffusion coefficients are also needed for developing an understanding of the relationship between the structure and transport properties of liquids and melts. However, earth-based measurements of interdiffusion coefficients in liquids are not easy to perform since diffusion profiles of composition are perturbed by natural convection which is caused by composition induced density changes. The solutal convection cannot be completely eliminated since it is intrinsically linked with compositional changes. One possible solution is to carry out experiments in zero-gravity environment. Another is to quantify and to account for the effect of solutal convection on interdiffusion composition profiles. Several quantitative analyses are available in the literature. To test these theoretical results, it is necessary to generate reliable experimental data in simple binary systems.

We have performed experiments in lead silicate supercooled melts (40 and 50 mol% PbO) since the diffusion profiles can be quenched to room temperature where they can be measured conveniently by electron analytical techniques. Two types of interdiffusion infinite couples with the interdiffusion direction same as the direction of gravity were annealed at 750 and 850° C for various times. In normal couples, the low density melt (40 mol % PbO) was on top and in inverted couples the high density composition (50 mol % PbO) was on top. No free convection is expected in the normal couples and these profiles can be used to obtain the true values of the diffusion coefficients. Free convection is expected in the inverted couples. The profiles for the inverted couples can be used to test the validity of the models.

In all (except one) experiments with inverted couples a complete inversion of the compositions was observed indicating that the Rayleigh-Taylor instability was dominant. The Rayleigh-Taylor instability describes the inversion of two immiscible liquids when the heavier one lies on top. However, one couple did not show inversion and was only in the early stages of Rayleigh-Taylor instability. We were able to measure the composition profiles in this couple at several different locations. The results and analysis of these experiments will be presented.

**Keywords:** interdiffusion, solutal convection, lead silicate melts, new research

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***ID#: 38***

**Polymosomes: Tough Giant Vesicles from Block Copolymers**

**Hammer, Daniel**

University of Pennsylvania

Abstract in Progress

## SECONDARY NEUTRON PRODUCTION FROM SPACE RADIATION INTERACTIONS: ADVANCES IN MODEL AND EXPERIMENTAL DATA BASE DEVELOPMENT

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For humans engaged in long-duration missions in deep space or near-Earth orbit, the risk from exposure to galactic and solar cosmic rays is an important factor in the design of spacecraft, spacesuits, and planetary bases. As cosmic rays are transported through shielding materials and human tissue components, a secondary radiation field is produced. Neutrons are an important component of that secondary field, especially in thickly-shielded environments. Calculations predict that 50% of the dose-equivalent in a lunar or Martian base comes from neutrons, and a recent workshop held at the Johnson Space Center concluded that as much as 30% of the dose in the International Space Station may come from secondary neutrons. Accelerator facilities provide a means for measuring the effectiveness of various materials in their ability to limit neutron production, using beams and energies that are present in cosmic radiation. The nearly limitless range of beams, energies, and target materials that are present in space, however, means that accelerator-based experiments will not provide a complete database of cross sections and thick-target yields that are necessary to plan and design long-duration missions. As such, accurate nuclear models of neutron production are needed, as well as data sets that can be used to compare with, and verify, the predictions from such models. Improvements in a model of secondary neutron production from heavy-ion interactions are presented here, along with the results from recent accelerator-based measurements of neutron-production cross sections.

An analytical knockout-ablation model capable of predicting neutron production from high-energy hadron-hadron interactions (both nucleon-nucleus and nucleus-nucleus collisions) has been previously developed. In the knockout stage, the collision between two nuclei result in the emission of one or more nucleons from the projectile and/or target. The resulting projectile and target remnants, referred to as prefragments, then decay by the emission of nucleons, composites, and gamma rays. Recent improvements to the model have incorporated coalescence effects, which effectively tie up single nucleons in the formation of composites during final-state interactions. Comparison of the improved model's predictions with neutron production data near 0° in the  $^{40}\text{Ca} + \text{H}$  reaction at 357 and 565 MeV/nucleon show marked improvement.

**Keywords:** cosmic radiation, secondary neutron production, knockout-ablation model, radiation

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## TWINNING, EPITAXY AND DOMAIN SWITCHING IN FERROELASTIC INCLUSION COMPOUNDS

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In this work we seek an understanding of the cooperative, elastic phenomenon of domain switching through comparison of physical properties and defect structures of a series of closely related inclusion compounds that undergo domain switching under applied anisotropic stress (ferroelasticity). These inclusion compounds are based upon the same urea channel framework, but they differ according to the orientation, dimensionality and cooperativity of specific hydrogen bonding networks. By growing crystals in the presence of tailor-made impurities, one can disrupt specific hydrogen bond networks and observe measurable changes in the kinetics and reversibility of the ferroelastic response. This comparative method therefore serves as a unique method for understanding the specific molecular mechanisms that control domain switching.

The ferroelastic inclusion compounds in question exhibit twinning, dislocations and other types of defect structures that can perturb the ferroelastic response. All of these can be studied with synchrotron white beam X-ray topography (SWBXT) in the presence or absence of external forces. To complement this technique we have purchased a Metripol microscope, which can be used to map the orientation and magnitude of the birefringence of a crystal.

For ferroelastic crystals, the orientation map reveals domain orientations directly. The retardation map contains further information about disorder within and between domains and can be used to identify the best regions of a crystal for crystal structure analysis. With *in situ* stress experiments, domain switching can be imaged directly and hysteresis loops can be generated. Since memory effects in these crystals are thought to be related to crystal perfection, this is a powerful method for identifying strained sites in crystals under stress.

This technique is especially useful for ferroelastic crystals in which the distortion from hexagonal metric symmetry is small (or zero with optically anomalous crystals). In such crystals, the birefringence is so small that ordinary light microscope techniques cannot be used to distinguish different sector orientations. In ferroelastic crystals of 2,19-eicosanedione/urea, for example, birefringence mapping reveals domain orientations quite readily. Because the distortion from hexagonal metric symmetry is so small in this crystal, ordinary rules of epitaxy do not apply, and domains that would ordinarily be mismatched can coexist on either side of a common domain wall.

**Keywords:** ferroelastic, inclusion compound, birefringence, twinning, epitaxy, new research

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# KINETIC MONTE CARLO SIMULATIONS OF ROD EUTECTIC GROWTH; THE SURFACE ROUGHENING TRANSITION OF BINARY ALLOYS

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Monte Carlo simulations have been used successfully to model steady state growth of rod eutectics from the melt. We are using a three dimensional kinetic Monte Carlo (kMC) model with diffusion by pair exchange only in the liquid phase. Entropies of fusion are first chosen to fit the surface roughness of the pure materials while the bond energies are derived from the equilibrium phase diagram with the choice of treating the solid and liquid as regular and ideal solutions respectively. Growth of the rods is initiated from columns of pure B material embedded in an A matrix, arranged in a close packed formation with semi-periodic boundary conditions. These simulations are conducted on a FCC lattice oriented in the  $\{100\}$  direction so that the faceting may exist out of the growth plane. The simulation cells typically have dimensions of 50 by 87 by 200 unit cells. Steady state growth has been compliant with the Jackson-Hunt model. In the kMC simulations using the spin-one Ising model, growth of each phase is faceted or non-faceted phases depending on the entropy of fusion.

While the surface roughening transition of single component systems have been studied, the surface roughening transition for binary systems have not. To better understand these systems we have conducted a study on the spin-one Ising Model with diffusion using kMC. We have observed that the surface roughness depends on the bond energies and melting temperature as given by the liquidus line on the equilibrium phase diagram. The surface roughness depends on the density of lateral bonds missing at the surface. The surface roughing transition, where the two-dimensional nucleation barrier disappears, is determined by height-height correlations. The location of the surface roughening transition for the phases of a eutectic alloy determines whether the eutectic morphology will be regular or irregular.

**Keywords: rod eutectics, eutectic growth, kinetic Monte Carlo, surface roughing, spin-one Ising model, theoretical**

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**EXPERIMENTAL AND NUMERICAL INVESTIGATIONS OF  
GROWTH MORPHOLOGIES OF PERITECTIC REACTIONS**

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Many engineering materials from steels to high temperature superconductors are produced from peritectic alloys, the properties and post-solidification processing of which are directly related their crystallization histories. The design of processes to control the microstructure and resultant properties of these materials requires knowledge of how the microstructure develops.

The research consists of processing experiments and calculations to study the developing morphology of peritectic reactions. Of particular interest is the coupled growth problem for peritectic systems. Cellular automata models are currently being developed to describe the morphological development during peritectic solidification. In these models, solid growth and solutal diffusion are calculated separately for each time step. Growth at each location is determined by examining the current states (phase, composition) of neighboring locations. The transition rules that determine the current and new state of a cell depend on local composition gradients and interface curvature. Solute rejected from newly formed solid is redistributed to the surrounding liquid and overall mass diffusion throughout the domain is calculated using an implicit finite volume scheme. Modeling the morphological development of solutal dendrites is currently being pursued, and the progress and problems associated with the introduction of a second solid phase will be discussed. The results of the numerical analysis will be compared to results from a series of directional solidification experiments. Directional solidification experiments are performed in an image furnace using compressed gas to cool the specimen and provide control of the thermal gradient. The growth morphologies obtained from the numerical and directional solidification experiments for different peritectic alloys systems will be discussed.

**Keywords: peritectic solidification, cellular automata, theoretical**

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**STUDIES OF PROPERTIES OF UNDERCOOLED GLASS FORMING METALLIC ALLOYS****W.L. Johnson\*, J. Schroers, and W.K. Rhim**

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Bulk metallic glass forming liquids are metal alloys which exhibit a high degree of resistance to nucleation and growth of crystals. Such alloys can be processed for laboratory time scales in the deeply undercooled liquid state. This has made studies of thermophysical properties of these liquids from the equilibrium melt down to the glass transition temperature of the undercooled melt. Of particular interest is the study viscosity and atomic diffusion in these glass forming liquids.

Electrostatic Levitation (ESL) Processing offer a platform for study liquids under high vacuum, containerless, and quiescent conditions. Using a NASA supported ESL facility located at Caltech, we have developed a method for laser heating and melting of spherical liquid drops under high vacuum conditions using high symmetry 4-beam tetrahedral laser heating. The liquid drop is melted, stably positioned, and subsequently brought to chosen temperature with very near isothermal conditions. A 3mm sphere can be maintained at 1000 K with total temperature variations of order or less than 0.1 K over the sphere. Under such conditions, both gravity driven and Marangoni convection within the liquid sphere can be minimized. Steady state convective flow velocities of microns per second and less can be achieved. The liquid thus exhibits “benchmark” levels of quiescence. The “near quiescence” of the liquid allows, for the first time, direct measurements of intrinsic atomic diffusion constants and impurity diffusion constants in the liquid. The diffusants are deposited from the gas phase onto the surface of the levitated liquid drop and allowed to diffuse into the sphere. Depth profiles of the diffusant in the sphere are captured by relatively rapid “quenching” the sample from the measurement temperature to ambient and are later analyzed to obtain diffusion constants for the molten alloys.

Under microgravity conditions, g-driven convection can be mitigated still further to yield “benchmark” atomic diffusion measurements in liquids which are essentially “free” of convective contamination effects. Analysis of temperature distributions, Marangoni and g-driven convective flows, etc. will be presented in the talk along with experimental results for actual samples processed in the ground-based Caltech High Vacuum, Symmetric Heating, Electrostatic Levitation Facility. ESL data on actual glass forming liquids will be presented to illustrate time-temperature-processing windows for liquid diffusion studies in the shallow and deeply undercooled regimes of several glass forming alloys.

**Keywords: alloys, glass formation, atomic diffusion, electrostatic levitator, flight**

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**NANOLAYERED BIOMIMETIC COMPOSITES BASED ON COLLAGEN**

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We have been investigating collagen-like model oligopeptides as molecular bases for complex ordered biomimetic materials. The collagen-like molecules incorporate aspects of native collagen sequence and secondary structure. Designed modifications to native primary and secondary structure have been incorporated to control the nanostructure and microstructure of the collagen-like materials produced. We find that the collagen-like molecules form a number of “lyotropic rod” liquid crystalline phases, which because of their strong temperature dependence in the liquid state can also be viewed as “solvent intercalated thermotropic” liquid crystals. The liquid crystalline phases formed by the molecules can be “captured” in the solid state by drying off solvent, resulting in solid nanopatterned (chemically and physically) thermally stable (to > 100 C) materials. Designed sequences which stabilize smectic phases have allowed a variety of nanoscale multilayered biopolymeric materials to be developed. Preliminary investigations suggest that chemical patterns running perpendicular to the smectic layer plane can be functionalized and used to localize a variety of organic, inorganic, and organometallic moieties in very simple multilayered nanocomposites. The phase behavior of collagen-like oligopeptide materials will be presented, emphasizing the correlation between mesophase, molecular orientation, and chemical patterning at the microscale and nanoscale. In many cases, the textures observed for smectic and hexatic phase collagens are remarkably similar to the complex (and not fully understood) “helicoids” observed in biological collagen-based tissues. Comparisons between biological morphologies and collagen model liquid crystalline (and solidified materials) textures may help us understand the molecular features which impart order and function to the extracellular matrix and to collagen-based mineralized tissues. The peptides are synthesized by traditional methods. A number of the oligopeptides have been produced at high yield in vivo, suggesting that synthesis of molecules which form interesting materials can be scaled up, making a variety of potential applications feasible.

**Key words: collagen, self-assembly, liquid crystalline, nanocomposite, biomaterials**

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# PHASE-FIELD SIMULATIONS OF THREE-DIMENSIONAL DENDRITIC GROWTH AT LOW UNDERCOOLING

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We report the results of phase-field simulations of equiaxed dendritic growth that focus on obtaining a detailed characterization and fundamental understanding of the initial stage of sidebranching behind the growing tips of primary branches. These simulations exploit several analytical and computational improvements of the phase-field approach that allow us to simulate quantitatively dendritic evolution in three-dimensions in the presence of thermal fluctuations. We are therefore able to test for the first time the predictions of the sharp-interface noise-amplification theory with purely diffusive heat transport, and to make comparisons with microgravity benchmark experiments.

The growth dynamics is simulated for different undercoolings and anisotropy values. The sidebranching activity is studied by recording time traces of the  $x$  coordinate of the interface in the (100) plane for different distances  $z$  from the tip along the growth axis. We compute from these traces two quantities: (i) the root-mean-square sidebranch amplitude  $A = [\langle x(z,t)^2 \rangle - \langle x(z,t) \rangle^2]^{1/2}$  where  $\langle \rangle$  denotes a time average over a time interval  $t$ , and (ii) the mean spacing between sidebranches defined as  $\langle \lambda(z) \rangle = 2Vt / N(z)$  where  $N(z)$  is the number of extrema of  $x(z,t)$  (i.e. zero crossings of  $dx(z,t)/dt$ ) during the same time interval. Given the computing time available for each run, we are able to study time intervals where  $N$  is about 20, which is just sufficient to obtain statistically meaningful averages.

We find that, remarkably, thermal fluctuations of microscopic origin suffice to produce the level of sidebranching activity observed experimentally, which is the first direct confirmation of this hypothesis. Our results show that both the distance from the tip at which sidebranches become visible and their mean spacing decrease with decreasing anisotropy. Both of these trends are qualitatively consistent with what is experimentally observed and predicted by noise-amplification theory. Furthermore, the several orders of magnitude exponential increase of the sidebranch amplitude with  $z$  is reasonably well predicted quantitatively by this theory. The variation of the mean sidebranch spacing with  $z$ , however, is not. In the simulations,  $\langle \lambda(z) \rangle$  increases steeply over a distance of a few  $\rho$  and then reaches a plateau after passing through a maximum that is more pronounced for lower anisotropy. In contrast, theory predicts a smooth monotonous increase of  $\langle \lambda(z) \rangle$  with  $z$ . Possible limitations of this theory underlying this discrepancy are discussed.

**Keywords:** dendrites, sidebranching, noise, anisotropy, phase-field

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**STUDIES OF NUCLEATION AND GROWTH, SPECIFIC HEAT AND  
VISCOSITY OF UNDERCOOLED MELTS OF QUASICRYSTALS  
AND POLYTETRAHEDRAL-PHASE-FORMING ALLOYS**

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The local atomic structures of undercooled liquid metals are presumed to be icosahedral; this order is incompatible with translational periodicity, constituting a barrier to the nucleation of the crystal phase. The extended atomic structure of the icosahedral quasicrystal (i-phase) is similar to that presumed in the undercooled liquid. Therefore, a comparison of the maximum undercooling in alloys that form the i-phase with those that form crystal phases provides a probe of the liquid structure.

Ti-Zr-Ni alloys are well suited for these investigations. Phases of varying complexity form with small changes in the Ni concentration for alloys with similar Ti and Zr concentrations. A stable i-phase forms at low temperatures, raising the intriguing possibility that it might be the first ground-state quasicrystal. By correlating the amount of undercooling for these phases with measurements of the specific heats, viscosities, and diffraction-based structural observations of the undercooled liquids, the existence of icosahedral order and its influence on physical properties can be determined. The strong reactivity, high density, and low liquidus temperatures near the i-phase forming concentrations prohibit accurate measurements of these physical properties without containerless solidification.

We have made preliminary studies, using the electrostatic levitation facility (ESL), at NASA/Marshall Space Flight Center, that demonstrate the feasibility of the studies proposed for the International Space Station. We demonstrate metastable i-phase formation in alloys containing 21 at.% Ni, allowing the first studies of the difference in nucleation between two polytetrahedral alloys of similar composition (the i-phase and the C14). That the nucleation of the i-phase is even easier than for the C14 phase indicates that the local structure of the undercooled liquid is not simply polytetrahedral, but is actually more similar to that of the icosahedral phase. An increasing order in the liquid with undercooling is supported by ESL-based measurements of the specific heat and viscosity and by x-ray diffraction studies made by aerodynamic and electrostatic levitation of liquid alloy droplets on the Advanced Photon Source located at Argonne National Laboratory.

**Keywords: undercooling, nucleation, liquid structure, specific heat, viscosity, flight**

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**MONODISPERSE LIGAND STABILIZED GOLD NANOPARTICLES.  
UNDERSTANDING THE EFFECTS OF DIFFERENT LIGANDS.**

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It is proposed that new types of crystalline materials could be grown in perfect shapes in microgravity. Especially promising are nanocrystal superlattices (NCSLs) based on gold, since gold is heavy and can readily be prepared in ligand stabilized nanocrystalline form. However in order to bring this idea to fruition better synthetic methods for preparing large amounts of cleanly monodisperse gold nanocrystals must be devised. This led to the discovery of a digestive ripening process. Indeed, we have found that heating a metal containing colloid at or near the solvent boiling point in the presence of a surface active ligand, is an extremely efficient procedure to prepare highly monodisperse colloids. This process has been called digestive ripening, and the usefulness of thiols as digestive ripening agents has already been established. In an effort to find alternative digestive ripening agents we have now used alkyl- amines, silanes, phosphines and halides. Amines and silanes were found to be similarly efficient for this purpose. The important steps involved in the digestive ripening have been identified as i) breaking the polydisperse colloid into a much smaller nanoparticles, ii) isolating these smaller particles from reaction side products, and iii) refluxing the isolated small nanoparticles in the presence of the ligand. The success of a ligand as a good digestive ripening agent is based on its capacity to break the bigger nanoparticles into smaller ones in the first step and its ability to adhere to the nanoparticle surface while the reaction side products are being removed in the second step. Though most of the ligands do a reasonably good job in the first step, some fail in the second step rendering them ineffective as digestive ripening agents. The similarities between the successful digestive ripening ligands will be discussed in detail. It was also found that irrespective of the head group, ligands with shorter alkyl chain lengths favor 3D ordering of the resulting monodisperse colloids while those with longer alkyl chain lengths lead to 2D lattices. The reasons for this are explained based on the decreasing van der Waals attraction between the gold particles as the distance between them is increased through the alkyl chain length of the capping ligand.

**Keywords:** nanocrystal superlattice, microgravity, ripening, monodisperse, ligand, gold, nanostructures

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**DATA AND MODELING OF DENDRITES  
SUBJECT TO A STEP CHANGE IN PRESSURE (TDSE)**

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There is considerable interest in dendritic solidification because of the influence dendrites have in the determination of microstructure, and thereby in the physical properties of cast metals and alloys. Current theories and models of dendritic growth generally couple diffusion effects in the melt with the physics of the interface. Data and subsequent analysis prior of the tip growth speed and radii of thermal succinonitrile dendrites in the near-convection free, on-orbit, free-fall environment demonstrate that these theories yield predictions that are reasonably in agreement with the results of experiment. However, data and analysis for assessing the interfacial physics component of theory are not sufficiently detailed or definitive. To study fundamental aspects of dendritic interface stability, we are measuring and modeling the kinetics and morphology of dendrites as they evolve from one well-defined steady state at a pre-set supercooling, through a transient stage, to a different well-defined steady state.

More specifically, we subject succinonitrile dendrites, growing under steady-state conditions, to a rapid change in pressure. This leads to a rapid change in thermal driving force from the corresponding change in both the equilibrium melting temperature due to the Clapeyron effect, and a change in the far-field temperature due to adiabatic temperature changes in the bulk liquid and solid. Subsequently, we observe transforming from a well-characterized initial state into a new steady-state. Initial data reveal that the dendrite tip velocity changes almost as fast as the pressure charges, while the tip radius changes occur more slowly, taking from 10 – 60 seconds depending on the size of the step change and the final supercooling. Computer modeling of this process shows both agreements and disagreements with the experimental data. In making these observations and measurements, we are gaining new understandings of interfacial dynamics and state-selection physics.

**Keywords: dendrite, solidification, microstructure, interfacial, Clapeyron, flight**

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## STRUCTURE PROPERTY CORRELATIONS AND PHASE TRANSITIONS IN GROUP IV AND III-V LIQUIDS

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Prior molecular dynamics (MD) simulations and laser pulse-heating studies on amorphous Si indicate that Si, Ge, and III-V liquids may undergo a first-order liquid-liquid phase transition. For Si and Ge, this transition is predicted in the deeply supercooled liquid. Group III-V liquids are expected to exhibit the transition closer to their respective melting temperatures. The MD simulations predict that the transition occurs from the metallic liquid to a tetrahedrally-coordinated, viscous and semiconducting liquid. The models also predict a decreasing coordination of Si atoms as the liquid is supercooled towards the transition temperature. However, no direct experimental characterization of the low-coordination phases has been obtained. The purpose of this ground-based research program is to: (1) search for and independently confirm the existence of such first-order transitions, and (2) determine the liquid phase structures.

This experimental research program is based on the use of conical nozzle levitation techniques to study the supercooled liquid phases, combined with x-ray diffraction experiments to investigate structural changes in the liquid. The structural results were obtained in four experimental campaigns at the Advanced Photon Source (APS) using the synchrotron x-ray source. Total and partial x-ray structure factors were obtained as a function of temperature and composition over a wide range of Q (momentum transfer) for liquids in the normal and supercooled states. The range of materials studied include silicon, Si-Ge alloys, GaSb, and InSb, YAG, and a number of materials of interest to other NASA PIs. At this conference, results will be presented on liquid Si, Si-Ge alloys, and GaSb alloys. The results obtained on silicon are particularly interesting; the structure factor and pair correlation functions were measured for liquid Si from 1420K (260K below melting point) to approximately 1800K. The data show that the Si coordination decreases from approximately 6.4 at 1800K to about 5 in the deeply supercooled liquid. There is an accompanying decrease in the mean interatomic distance (Si-Si) suggesting an increase in the density of the liquid with supercooling. These new measurements are in excellent agreement with our earlier results (which did not span such a wide temperature range) and confirm the predictions of the MD simulations. X-ray measurements on liquid SiGe were obtained over a 200K temperature range including the supercooled regime; a decrease in first-shell coordination is also observed for this case in addition to a shift to larger interatomic distances in the first coordination shell.

**Keywords: liquid silicon, phase transitions, x-ray diffraction, supercooling, characterization**

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**DEFECT, KINETICS AND HEAT TRANSFER OF CDTE  
BRIDGMAN GROWTH WITHOUT WALL CONTACT**

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Prior space experiments have suggested that the defect (twin and dislocation) density can be dramatically reduced if the crystal can grow without wall contact. Techniques have been proposed to promote wall detachment during solidification by Larson, Duffar, Szofran, and Wilcox. We adopt an ampoule with a soft-finned Carbon inner wall, which can arrange for growth virtually free from wall contact. An integrated transport model for detached solidification has been developed to combine a global heat transfer/phase-change model for Bridgman growth with a meniscus instability model near the wall. The integrated model is used to design apparatus and find the optimal geometry and operating conditions for detached solidification of CdTe growth in space and on the ground.

Our experiment concept is to grow a CdTe crystal in a soft-wall ampoule made of Carbon velvet, with a uniform inner diameter. Crystal growth in conventional ampoules and ampoules with soft walls will be conducted and results will be compared in order to understand the detached solidification process and impact on crystalline structural quality. A global transport model has been developed which accounts for heat transfer in the multiphase system (solid, liquid and gas), gravitational and Marangoni melt convection, and transport of dissolved gas. Location and dynamics of the solidification interface are accurately tracked by a multizone adaptive grid generation scheme. The fluid mechanics and heat transfer in the three-phase system have been considered, including dynamical movement of the solidification interface and meniscus. A wall contact model has been developed which accounts for the meniscus shape and dynamics, and instability of the free surface. The integrated model is used to study the effects of the space between Carbon velvet fins, the size and shape of the fin, and wettability of the fin on the dewetting of the melt and heat transfer of the melt and furnace. The geometric configuration of a modified Bridgman furnace has been designed to promote dewetting of the melt and detached solidification. The finned Carbon wall is modeled using straight fins of uniform cross section. The heat transfer of the fins is solved analytically for a single fin and modeled for interaction between the fins. The anisotropy of thermal conductivity is considered in the simulation.

**Keywords: directional solidification, Bridgman crystal growth, defects, wall contact, new research**

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**NANOPARTICLE ENGINEERING OF COMPLEX FLUID BEHAVIOR****Jennifer A. Lewis\***

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A new mechanism for regulating the stability of colloidal particles has been discovered. Negligibly charged colloidal microspheres, which flocculate when suspended alone in aqueous solution, undergo a remarkable stabilizing transition upon the addition of critical volume fraction of highly charged nanoparticle species. Zeta potential analysis revealed that these microspheres exhibited an effective charge buildup in the presence of such species. Scanning angle reflectometry measurements indicated these nanoparticle species did not adsorb on the microspheres under the experimental conditions of interest. It is therefore proposed that highly charged nanoparticles segregate to regions near negligibly charged microspheres due to their repulsive Coulombic interactions in solution. This type of nanoparticle haloing provides a new method for tailoring the behavior of complex fluids, including its flow properties and structure.

**Keyword: new research**

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**MAGNETIC FIELD EFFECTS ON CONVECTION AND SOLIDIFICATION IN NORMAL AND MICROGRAVITY**

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It has well understood that convective flows induced by g-jitter forces associated with spacecraft are responsible for defects formation and irregularity in product quality during melt growth of single crystals in microgravity. This presentation discusses the numerical models and experimental measurements developed towards a fundamental understanding of the g-jitter induced fluid flows and their effects on solidification in microgravity with and without the presence of additional damping forces that are derived from the applied DC magnetic fields. The numerical models are developed using both the analytical and numerical methods, with the former intended to provide an order of magnitude estimate and the latter to more accurate representation of the melt flow and solute redistribution with and without magnetic damping. The numerical models include both 2-D and 3-D transient fluid flow, heat transfer, mass transfer and solidification under the combined action of g-jitter and magnetic fields. The models are developed using the finite element method. Various numerical techniques, such the dissection of global matrices and parallel algorithms, are applied to bring down the otherwise prohibitive computational costs to a reasonable level, in particular for transient 3-D computations. In some cases, a factor of 120 speed-up is achieved. In accordance with the numerical model development, a ground-based thermal oscillator is established to simulate the g-jitter driven flows and measurements were taken for a wide range of conditions. Numerical simulations using both the 2-D and 3-D models are conducted for both idealized, synthesized and real g-jitter forces, and are tested against the experimental measurements taken on the thermal oscillator. Results show that the numerical model predictions compare well with the measurements. Analysis of these results illustrates that an applied magnetic field can have a drastic influence on the convective flows induced by g-jitter and can be particularly useful to suppress the effects resulting from the spiking of g-jitter signatures, which are considered the most detrimental effects on quality of crystals grown in space.

On the other front, we have continued on our effort on the study of flow and surface deformation of melt droplets in electromagnetic and electrostatic levitators. The numerical models have been and case studies have been carried out for melt flow and surface deformation in these droplets induced by either electromagnetic forces in the case of magnetic levitation or the surface tension in the case of electrostatic levitation. These models have been used to help other NASAPIs with their research on facility development and experiment planning and interpretation of the experimental measurements.

**Keywords: magnetic damping, g-jitter induced convection, solidification, electromagnetic levitation, electrostatic levitation.**



# MODELS OF MASS TRANSPORT DURING MICROGRAVITY CRYSTAL GROWTH OF ALLOYED SEMICONDUCTORS IN A MAGNETIC FIELD

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Recent rapid advances in optoelectronics have led to a great demand for more and larger alloyed semiconductor crystals, such as germanium-silicon and various II-VI alloyed crystals, with fewer dislocations and other microdefects and with more uniform and controllable compositions. Currently, high-quality crystals of these alloys can be grown by epitaxial processes, but the time required to grow a certain amount of single crystal is roughly 1,000 times longer than the time required for Bridgman growth from a melt. Unfortunately some crystals grown from the melt in space still have unacceptable segregation, for example, due to residual accelerations. The application of a weak magnetic field during crystal growth in space may eliminate the undesirable segregation.

Our initial research has primarily been focused on models which investigate the effect of a magnetic field on segregation in an alloyed crystal on Earth. The numerical treatment of transient species transport is difficult because there are extreme differences between the time scales for the diffusions of internal energy, momentum and species, and there are thin species-diffusion or viscous boundary layers for every value of the field strength. Therefore, the simultaneous time integration of the full Navier-Stokes, internal energy, and species transport equations must always have a very fine spatial grid and a very small time step so that only a few minutes of crystal growth can be simulated. Using asymptotic methods, we have provided a significant reduction in the number of computations needed to accurately simulate the entire growth process in a magnetic field, and have published predictions of solutal convection and the segregation in the entire crystal for an alloyed semiconductor grown in a magnetic field by the Bridgman process. Future research involves developing models which investigate the effects of the microgravity environment on segregation in the alloyed crystal grown in a magnetic field. The models involve using asymptotic approximations which are appropriate for the reduced convective flows in microgravity and for the magnetic fields that will be used in microgravity.

Other research projects which have been supported under this grant include analytical and numerical modelling of (1) melt motions during floating-zone growth of high-purity silicon crystals in steady and rotating magnetic fields, (2) mass transport during horizontal Bridgman growth of doped semiconductors in steady magnetic fields, and (3) dopant transport during liquid-encapsulated growth of compound semiconductor crystals in a magnetic field.

Supported by NASA Microgravity Research Division.

**Keywords:** crystal growth, magnetic fields, modeling, new research

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**NOVEL MICROSTRUCTURES FOR POLYMER-LIQUID CRYSTAL  
COMPOSITE MATERIALS**

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Polymer/liquid crystal composites are a scientifically rich and varied class of technologically important materials, in which the partial ordering and fluidity of liquid crystals and the spatial organization inherent in polymers must coexist. Efforts to exploit the anisotropic optical, electrical and mechanical properties of polymer/liquid crystal composites have been pursued in the context of the so-called polymer dispersed liquid crystals (PDLCs), biphasic materials in which micron-sized droplets of minority-phase liquid crystals are dispersed in a polymeric medium, and the polymer-stabilized liquid crystals (PSLCs), gels in which a liquid crystal is stabilized by a tenuous polymer network. Despite a significant level of effort, it has proven difficult to obtain PDLCs and PSLCs having optimized electro-optic properties needed for flat panel display technology. Consequently a novel family of polymer/liquid crystal composite materials may be more suitable for display technology, namely dispersions of polymer colloidal particles in liquid crystal media (liquid crystal dispersed colloids, or LCDCs).

For both PDLCs and LCDCs, a significant volume fraction of the materials is associated with the interfacial region between the two phases. Therefore understanding and control over the polymer/liquid crystal interface is key to the optimization of electro-optic properties. For this reason, a new bead-necklace model of liquid crystal molecules has been developed. This model has enough detail to incorporate important liquid crystal molecular parameters such as flexibility and chirality, and yet the model is simple enough to allow highly accurate molecular dynamics computer simulations of liquid crystal interfaces. Results will be shown that demonstrate that the model is perhaps the first that is capable of predicting the effects of temperature and pressure on the phase diagram of a liquid crystal in a realistic way.

**Keywords: liquid crystals, surface tension, molecular dynamics, interfaces, microstructure, new research**

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## CO<sub>2</sub> ACQUISITION MEMBRANE (CAM)

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The objective of CAM is to develop, test, and analyze thin film membrane materials for separation and purification of carbon dioxide (CO<sub>2</sub>) from mixtures of gases, such as those found in the Martian atmosphere. The membranes are targeted toward *In Situ Resource Utilization (ISRU)* applications that will operate in extraterrestrial environments and support future unmanned and human space missions. A primary application is the Sabatier Electrolysis process that uses Mars atmosphere CO<sub>2</sub> as raw material for producing water, oxygen, and methane for rocket fuel and habitat support. Other applications include use as an inlet filter to collect and concentrate Mars atmospheric argon and nitrogen gases for habitat pressurization, and to remove CO<sub>2</sub> from breathing gases in *Closed Environment Life Support Systems (CELSS)*.

CAM membrane materials include crystalline faujasite (FAU) zeolite and rubbery polymers such as silicone rubber (PDMS) that have been shown in the literature and via molecular simulation to favor adsorption and permeation of CO<sub>2</sub> over nitrogen and argon. Pure gas permeation tests using commercial PDMS membranes have shown that both CO<sub>2</sub> permeance and the separation factor relative to other gases increase as the temperature decreases, and low  $\Delta P_{\text{CO}_2}$  favors higher separation factors. The ideal CO<sub>2</sub>/N<sub>2</sub> separation factor increases from 7.5 to 17.5 as temperature decreases from 22 °C to −30 °C. For gas mixtures containing CO<sub>2</sub>, N<sub>2</sub>, and Ar, plasticization decreased the separation factors from 4.5 to 6 over the same temperature range. We currently synthesize and test our own Na<sup>+</sup> FAU zeolite membranes using standard formulations and secondary growth methods on porous alumina. Preliminary tests with a Na<sup>+</sup> FAU membrane at 22 °C show a He/SF<sub>6</sub> ideal separation factor of 62, exceeding the Knudsen diffusion selectivity by an order of magnitude. This shows that the membrane is relatively free from large defects and associated non-selective (viscous flow) transport mechanisms.

The Membrane Test Facility (MTF) has been developed to measure membrane permeance over a wide range of temperature and pressure. The facility uses two volume compartments separated by the membrane that are instrumented to measure temperature, delta pressure across the membrane, and gas composition. A thermal shroud supports and encloses the membrane, and provides temperature control. Methods were developed to determine membrane permeance using the first order decay of the pressure difference between the sealed compartments, using the total pressure for pure gases, and partial pressure of each species in gas mixtures. The technique provides an end-to-end measurement of gas permeance that includes concentration polarization effects. Experiments have shown that in addition to membrane permeance properties, the geometry and design of associated structures play an important role in how membrane systems will function on Mars.

**Keywords:** zeolite, membrane, ISRU, Sabatier Electrolysis

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**DIFFUSION PROCESSES IN MOLTEN SEMICONDUCTORS (DPIMS):  
FLIGHT RESULTS FROM THE STS-94/MSL-1R SPACELAB MISSION**

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The Diffusion Processes in Molten Semiconductors (DPIMS) investigation was a three-part program that sought to:

- 1) Provide purely diffusive experimental measurements of the isothermal diffusion coefficients of gallium (Ga), antimony (Sb) and silicon (Si) in molten germanium (Ge) with sufficient accuracy and precision to:
  - a) Differentiate between model predictions of the temperature dependence.
  - b) Determine the effect of dopant size and type.
  - c) Determine if a “wall effect” was present.
  - d) Provide input to continuum model development.
  - e) Provide input to atomistic model development.
- 2) Develop a 2-dimensional, fully time dependent continuum numerical model of the germanium diffusion column, shear cell, cartridge and furnace for both earth-based and space-based experiments which accurately predicted the measured concentration profile as a function of distance in the diffusion column.
- 3) Develop an atomistic model that accurately predicts:
  - a) The purely diffusive isothermal diffusion coefficient of a dopant in a molten semiconductor.
  - b) The temperature dependence of the dopants in molten semiconductors.
  - c) Developed new empirical potentials useful for predicting other transport properties in molten semiconductor systems.

The efforts of the last two years have yielded outstanding results from all three parts of the DPIMS program. Despite numerous off nominal conditions, several of the diffusion experiments that were run on the MSL-1R Spacelab mission have yielded reliable diffusion coefficients. These diffusion coefficients are unexpectedly higher than those predicted from the Stokes-Einstein equation as well as those predicted by *ab-initio* computer modeling efforts. These diffusion coefficients were calculated using the ‘long-time’ solution to Fick’s second law from the measured concentration versus distance profile of the diffusion column. The concentration measurements were determined using Inductively Coupled Plasma- Mass Spectrometry (ICP-MS). A newly developed 3-parameter iterative solution technique combined with Monte Carlo simulations has allowed for a statistically accurate estimate of the error for these diffusion coefficients to be made.

**Keywords: flight samples, diffusion, dopants, semiconductors, modeling**

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## **NEUTRON SHIELDING EXPERIMENTS**

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We report on recent and planned experiments to determine high-energy neutron production in high-energy proton and heavy ion collisions with common and proposed spacecraft shielding materials and their combinations. Preliminary experiments with 20-800 MeV neutrons at Los Alamos and with 1 GeV/nucleon iron nuclei at the Brookhaven AGS have been completed. The analysis of the Los Alamos data has established the thick solid-state silicon detector calibration and response function. A small dual silicon detector telescope has been fabricated for unidirectional accelerator beams. Recent experiments with 10-20 MeV neutrons at Columbia RARAF and heavy ions at the BNL AGS will be reported. Experiments using high-energy protons are planned for 2002 and 2003.

**Keywords: neutrons, shielding, thick target collisions, radiation**

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**CONTROLLED SYNTHESIS OF NANOPARTICLES USING BLOCK COPOLYMERS:  
NANOREACTORS IN MICROGRAVITY CONDITIONS (NAG 8-1678)****Rigoberto C. Advincula, Juan Pablo Claude, and Jimmy W. Mays\***

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To achieve complete control of nanoparticle properties, it is necessary to obtain samples that are as close to monodisperse as possible. Polymers such as linear and star-linked poly(styrene)-block-poly(2-vinylpyridine) generate micelles in low polarity solvents like toluene, which can be used as reactors for the preparation of nanoparticles. We have established reliable synthetic routes for the preparation of CdS, CdSe, and Au nanoparticles within block copolymer micelles and within star-block copolymers.

In a typical CdS preparation, an methanol solution of  $\text{Cd}(\text{NO}_3)_2$  is added to the toluene solution of block copolymer, followed by the addition of  $\text{Na}_2\text{S}$  ( $[\text{Cd}^{2+}]/[\text{S}^{2-}] = 0.6$ ) and thioglycerol in methanol. Thioglycerol is an auxiliary capping agent that improves both the stability and monodispersity of the CdS nanoparticles. The particles obtained through this method have mean sizes of 10 nm for preparations using linear block copolymers, and 25 nm with star block copolymers. The particles show strong quantum confinement as seen in the absorption and emission spectra. The absorption spectra also indicate particle stability in solution for a minimum of 3 months. The necessity of polymer nanoreactors for the preparation of high quality particles is demonstrated by the emission spectra of CdS nanoparticles prepared with homopolystyrene and linear or star-linked poly(styrene)-block-poly(2-vinylpyridine). The yield and quality of CdS particles is greatly reduced if homopolystyrene is used, resulting in a weaker, broader, and blue-shifted emission. *Both the emission spectra and TEM micrographs suggest that the star-linked block copolymer is superior for the preparation of high quality particles.* This is probably due to enhanced micelle stability and homogeneity. We have also had great success in extending these synthetic routes to the preparation of CdSe and gold nanoparticles, where again the novel use of star-block copolymers is advantageous. In these cases, particles are prepared without the need of an auxiliary capping agent, which allows us to increase the concentration of reagents and the yield of the preparations. Furthermore, we have prepared gold nanoparticles in aqueous solution using a polyelectrolyte that possesses pendant reducing oligothiophene groups. Polyelectrolyte complex (PEC) with water-soluble terthiophene derivative was used for the reduction of  $\text{HAuCl}_4$  to gold nanoparticles. A number of parameters including solution concentration, percentage of complexation, solvent, reaction time, etc. were investigated in order to determine the extent of the reduction and nanoparticle formation (size, size distribution, etc.). This technique opens the possibility of combining electro- and optically-active materials with metal nanoparticles prepared *in-situ*.

In summary, we can reliably produce CdS, CdSe, and Au nanoparticles that are stable in solution for long times (at least three months). These particles are nano-sized (mean sizes typically 10-50 nm for semiconductors and as small as 4-8 nm for Au) and approximately spherical. The CdS and CdSe nanoparticles are very good emitters. Dilute solutions produce emissions clearly visible to the naked eye. The polydispersity is quite good, and the emission spectrum does not vary drastically with excitation wavelength. Thus, a major goal of this Earth-bound project has been achieved. The next step is to determine whether or not nanoparticle growth in a microgravity environment can further reduce the polydispersity of these materials.

**Keyword: nanostructures**\*Principal Investigator. email: [jmays@uab.edu](mailto:jmays@uab.edu)

# CONTROL OF MELT CONVECTION USING TRAVELING MAGNETIC FIELDS

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The crystal growth process is sustained by externally imposed thermal and solutal gradients. On earth, these gradients induce buoyancy convection in the melt which is often responsible for introducing undesired effects at the growth interface. A technique to counteract buoyancy, at least in the vicinity of the growth interface, may prove to be a valuable tool for understanding the relationship between convection and the introduction of defects into the crystal. It can also be valuable for industrial applications as the technique is fully understood and mastered. Presently, strong static magnetic fields are used for this purpose. A rotating magnetic field (RMF) is an example of a variable in time magnetic field and induces a primary swirling flow. A secondary meridional flow due to this swirl could counteract the buoyancy. However, the body force induced by RMF is perpendicular to the buoyancy force in the melt, thus the magnitude of the total force increases. On the contrary, the traveling magnetic field (TMF) is a direct way to induce a body force in the direction of gravity. Here one can adjust the magnitude of the force by adjusting the strength of the magnetic field not only to counteract the effects of buoyancy, but also to create conditions similar to varying levels of gravity. In this approach a number of coils are placed co-axially around the charge. The coils, carrying out-of-phase harmonic currents, induce a meridional (axial and radial) Lorentz force in the electrically conducting melt. The geometry of the coils, the phase differences between them, the currents, and the modulation frequency can be used to control the magnitude and to some extent the distribution of the force field in the melt. For a long cylindrical geometry, TMF is an ideal method of mixing or homogenizing electrically conducting melts. We have experimentally demonstrated its efficiency. Fluid dynamics modeling of a TMF induced flow demonstrated a significant level of control of convective flow in the molten zone of a crystal growth ampoule. In particular, for short melt columns, such as used in float zone or traveling heater methods, a 40 times reduction of the global flow level can be achieved. In case of Vertical Bridgeman, a 10-fold reduction can be obtained. Although a perfect stagnant melt is not achievable, the convective roll direction can be changed. This is quite attractive for experimental investigations. Another direction of this research is focused on the flow stability. Here we need to know the steady flow boundaries and characteristics of the first bifurcation in the system. Our initial calculations indicate that the critical values for the magnetic Taylor number are in the area of  $10^6$  for the aspect ratio of 1, and  $10^4$  for the aspect ratio of 10, quite similar to RMF values. Details of numerical modeling will be presented at the conference.

**Keywords:** convection, control of convection, magnetic field, magnetohydrodynamics, new research

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## CONVECTIVE AND MORPHOLOGICAL INSTABILITIES DURING CRYSTAL GROWTH

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Linear morphological stability theory describes the conditions under which a smooth crystal-fluid interface becomes unstable, leading to cellular or dendritic growth and solute inhomogeneities in the crystal. The original treatment of morphological stability by Mullins and Sekerka assumed local equilibrium at the crystal-melt interface and isotropy of the crystal-melt surface tension; this is an excellent approximation for many metals growing from the melt at low growth velocities. There have been many extensions of the theory in order to elucidate the role of external fields and additional physical effects on the stability demarcation. We present recent research on temperature-dependent solute diffusivity, electrical effects, anisotropic kinetics, and shear flows.

In collaboration with S. Van Vaerenbergh, the effect of a temperature-dependent diffusion coefficient on the morphological stability of a binary alloy during directional solidification has been determined. Specific calculations are carried out for a tin-silver alloy. Although the temperature dependence of the diffusion coefficient has little effect on the critical concentration for the onset of instability, it causes a significant change in the wavelength at the onset of instability.

Electrical currents can modify the crystal growth process and affect morphological stability. Current pulsing is used to demarcate the solid-melt interface. The solute segregation associated with current pulsing has been measured by Dabo et al. in bismuth-antimony alloys and compared with a numerical model. A perturbation analysis is possible for small pulses, and clarifies the behavior of the interface velocity during the pulse.

In collaboration with A. Chernov, the effect of anisotropy of interface kinetics on morphological stability during growth from a supersaturated solution has been treated. The kinetic anisotropy arises from a model of step motion in which the morphological instability corresponds to the clustering of elementary steps, leading to step bunching. Kinetic anisotropy causes traveling waves along the crystal-solution interface and an enhancement of morphological stability. A shear flow opposite to direction of the step motion also enhances morphological stability, while flow in the same direction is destabilizing. An oscillating flow may enhance stability, and this possibility has been studied using Floquet theory.

**Keywords:** morphological stability, temperature-dependent diffusivity, Peltier pulsing, anisotropic interface kinetics, shear flows, theoretical

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## INVESTIGATION OF DYNAMIC OXYGEN ADSORPTION IN MOLTEN SOLDER JETTING TECHNOLOGY

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Surface tension forces play a critical role in fluid dynamic phenomena that are important in materials processing. The surface tension of liquid metals has been shown to be very susceptible to small amounts of adsorbed oxygen. Consequently, the kinetics of oxygen adsorption can influence the capillary breakup of liquid-metal jets targeted for use in electronics assembly applications, where low-melting-point metals (such as tin-containing solders) are utilized as an attachment material for mounting of electronic components to substrates. By interpreting values of surface tension measured at various surface ages, adsorption and diffusion rates of oxygen on the surface of the melt can be estimated.

This research program investigates the adsorption kinetics of oxygen on the surface of an atomizing molten-metal jet. A novel oscillating capillary jet method has been developed for the measurement of dynamic surface tension of liquids, and in particular, metal melts which are susceptible to rapid surface degradation caused by oxygen adsorption. The experimental technique captures the evolution of jet swells and necks *continuously* along the jet propagation axis and is used in conjunction with an existing linear, axisymmetric, constant-property model to determine the variation of the instability growth rate, and, in turn, surface tension of the liquid as a function of surface age measured from the exit orifice. The conditions investigated so far focus on a time window of 2–4ms from the jet orifice. The surface properties of the eutectic 63%Sn-37%Pb solder alloy have been investigated in terms of their variation due to O<sub>2</sub> adsorption from a N<sub>2</sub> atmosphere containing controlled amounts of oxygen (from 8 ppm to 1000 ppm). The method performed well for situations where the oxygen adsorption was low in that time window. The value of surface tension for the 63Sn-37Pb solder in pure nitrogen was found to be 0.49 N/m, in good agreement with previously published work. A characteristic time of O(1ms) or less was determined for the molten-metal surface to be saturated by oxygen at 1000 ppm concentration in N<sub>2</sub>.

The study also involves the performance of drop-tower experiments in the microgravity facilities of the NASA Glenn Research Center. The main elements of the experiment rig needed for the reduced-gravity tests have been constructed and include an environmental chamber, a power distribution module, a computer-based data acquisition system, and a high-speed visualization system. Conducting experiments in reduced gravity allows the experimental investigation of large-diameter jets in conjunction with the surface tension measurement technique described above.

**Keywords:** surface tension, liquid Sn-Pb solder, capillary jet, oxygen adsorption, new research

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**RADIATION TRANSPORT PROPERTIES OF POTENTIAL IN SITU-DEVELOPED  
REGOLITH-EPOXY MATERIALS FOR MARTIAN HABITATS**

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Mission crews in space outside the Earth's magnetic field will be exposed to high energy heavy charged particles in the galactic cosmic radiation (GCR). These highly ionizing particles will be a source of radiation risk to crews on extended missions to the Moon and Mars, and the biological effects of and countermeasures to the GCR have to be investigated as part of the planning of exploration-class missions. While it is impractical to shield spacecraft and planetary habitats against the entire GCR spectrum, biological and physical studies indicate that relatively modest amounts of shielding are effective at reducing the radiation dose. However, nuclear fragmentation in the shielding materials produces highly penetrating secondary particles, which complicates the problem: in some cases, some shielding is worse than none at all. Therefore the radiation transport properties of potential shielding materials need to be carefully investigated. One intriguing option for a Mars mission is the use of material from the Martian surface, in combination with chemicals carried from Earth and/or fabricated from elements found in the Martian atmosphere, to construct crew habitats. We have measured the transmission properties of epoxy-Martian regolith composites with respect to heavy charged particles characteristic of the GCR ions which bombard the Martian surface. The composites were prepared at NASA Langley Research Center using simulated Martian regolith, in the process also evaluating fabrication methods which could lead to technologies for *in situ* fabrication on Mars. Initial evaluation of the radiation shielding properties is made using radiation transport models developed at NASA-LaRC, and the results of these calculations are used to select the composites with the most favorable radiation transmission properties. These candidates are then evaluated at particle accelerators which produce beams of heavy charged particles representative in energy and charge of the radiation at the surface of Mars. We will present nuclear fragment spectra for regolith-epoxy composites and for some of their elemental components; the latter measurements are made to improve the accuracy of the models.

**Keywords: radiation protection, GCR, heavy ions, ISRU, Martian regolith**

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**SPACE- AND GROUND-BASED CRYSTAL GROWTH USING A BAFFLE (CGB)****C. Marin, T. Cummings, A. Curilov, and A.G. Ostrogorsky\***

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CGB is the parent investigation to the Microgravity Science Glovebox Investigation “SUBSA” which is scheduled for launch on May 31, 2002. The CGB investigation aspires to eliminate buoyancy driven convection and thus enable reproducible diffusion-controlled crystal growth in space and on earth. The key goals are: (i) obtain a better understanding of the role of convection in formation of inhomogeneities and crystalline defects; (ii) explore solidification phenomena that are obscured by convection; (iii) develop models of the transport processes occurring in solidification; (iv) seek explanations for previous space experiments which did not result in the diffusion-controlled segregation; and (v) measure diffusion coefficients of several dopants.

The focus of the work presented is modification of the existing SUBSA hardware, to meet the scientific goals of the CGB investigation. These modifications include a motor-driven baffle and a higher temperature in the hot zone, to allow growth of Ge and GaSb. Our numerical simulations indicate that Ge and GaSb crystals can be grown in SUBSA thermal chamber with about 300 W of heating power. Therefore, with small modifications of SUBSA hardware, the scientific goals of the CGB investigation could be realized through re-flight experiments in MSG. Using modified SUBSA hardware for the CGB investigation, would result in a significant reduction in cost and preparation time.

To demonstrate that SUBSA hardware can be used for the CGB investigation, a small “model” ground unit furnace was developed at RPI. The ampoule is driven by a linear stepping motor, using a combination of National Instrument’s Lab View and Intelligent Motion System’s IM483 micro-stepping driver. Each micro-step results in 0.05  $\mu\text{m}$  of linear displacement, yielding smooth steady solidification rate. The baffle is stationary with respect to the thermal chamber, while the ampoule driven linear stepping motor, moves the crystal and the melt relative to the fixed axial gradient.

The design of the RPI model furnace and the preliminary experimental results will be presented. This furnace will be used to grow doped Ge and GaSb crystals under terrestrial gravity and under strong magnetic fields.

**Keywords: crystal growth, convection, Ge, GaSb.**

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**SOLIDIFICATION USING A BAFFLE IN SEALED AMPOULES (SUBSA)**

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Solidification Using a Baffle in Sealed Ampoules (SUBSA) will be the first materials science experiment conducted in the Microgravity Science Glovebox (MSG) Facility at the International Space Station (ISS) Alpha. The launch is scheduled for May 31, 2002. Using the specially developed furnace, 10 Te and Zn-doped single crystals of InSb will be directionally solidified in microgravity. A key goal of the SUBSA investigation is to (i) clarify the origin of the melt motion in space laboratories and (ii) to reduce the magnitude of the melt motion to the point that it does not interfere with the transport phenomena. These goals will be accomplished through a special ampoule and furnace design. A disk-shaped baffle, positioned close to the freezing front, is used to reduce melt motion. Furthermore, the solidification will be visualized by using a transparent furnace, with a video camera, continuously sending images to the earth. This allows detection of bubbles and melt de-wetting that could cause surface tension driven convection.

In preparation for the space experiments, 30 ground-based experiments were conducted. The results of ground based tests and numerical modeling will be presented. Based on numerical modeling, 12 mm ID silica ampoules were selected. The small diameter ampoule favors closer placement of the baffle to the interface, without excessive radial segregation caused by forced convection while providing more damping of natural convection. The parts in the silica ampoule include 2 carbon springs made by Energy Science Laboratories, Inc., a pyrocarbon-coated graphite cylinder, pyrocarbon-coated graphite a baffle with the shaft and the InSb charge with the seed crystal grown by W.A. Bonner of Crystallod Inc.

**Keywords: crystal growth, convection, Glovebox, InSb.**

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## ANALYSIS OF CONTAINERLESS SOLIDIFICATION MICROSTRUCTURES IN UNDERCOOLED MELTS AND COMPOSITE SYSTEMS

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The main research objective is the evaluation and analysis of the undercooling and resultant solidification microstructures in containerless processing, including drop tube processing and levitation melt processing of selected alloys and composites. The results are intended for use as an experience base for the design of space-based microgravity experiments.

Containerless processing in ground-based drop tubes simulates microgravity conditions via solidification of liquid samples under free fall conditions. The containerless environment is also attained in levitation melt processing and removes a major source of impurities and heterogeneous nucleation sites, allowing for a large melt undercooling. This enhanced liquid undercooling exposes alternate solidification pathways, allowing for the formation of novel microstructures. Controlling the undercooling level provides some control of the operative solidification pathway and the resultant microstructure. The novel structures that may be produced in a ground-based containerless processing facility preview the wide range of possible materials processing experiments that may be conducted in a space-based laboratory. The results of the ground based study will be used to identify critical experimental variables in microgravity processing and the analysis can be used to design and define the science and hardware requirements for extended duration space experiments.

The current ground based studies have established that undercooling levels (exceeding 200 K in some systems) can be achieved in the model composite systems Ni/Ta<sub>2</sub>O<sub>5</sub>, Cu/Ta<sub>2</sub>O<sub>5</sub>, and Cu/Al<sub>2</sub>O<sub>3</sub>. These materials also provide a suitable means to study the interaction of free dendrites with incorporated particles at growth velocities on the order of meters per second. The critical velocities for incorporation in these composite systems are over three orders of magnitude higher than the critical velocities predicted by current models based on a planar solidification front. Detailed studies of the effects of interface velocity and alloy composition are now in progress to yield a clear understanding of the particle/dendrite interactions that is needed to develop a more complete analytical models. Modeling of the thermal analysis signals during solidification is being used to examine the changes in interface velocity during recalescence. These studies will provide guidance for future space experiments where the incorporation behavior can be analyzed under various conditions in the absence of the confounding influence of convection. The combination of ground-based studies and experiments under microgravity conditions will provide an understanding of the key parameters of the particle incorporation process that can lead to improved composite processing strategies.

**Keywords:** undercooling, solidification, microstructure, composite materials, new research

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**MONTE CARLO METHODS IN MATERIALS SCIENCE BASED ON FLUKA AND ROOT**

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A comprehensive understanding of mitigation measures for space radiation protection necessarily involves the relevant fields of nuclear physics and particle transport modeling. One method in particular is Monte Carlo analysis, a subject that has been evolving since the very advent of nuclear reactors and particle accelerators in experimental physics. Countermeasures for radiation protection from neutrons near nuclear reactors, for example, are as old as nuclear physics itself and Monte Carlo methods quickly adapted themselves to this field of investigation.

The study discussed here is concerned with taking the latest tools and technology in Monte Carlo analysis and adapting them to materials science applications such as radiation shielding design for the exploration of space, as well as investigating how next-generation Monte Carlos can complement the existing analytical methods used by NASA. We will discuss our Monte Carlo of choice, a program known as FLUKA (German acronym for FLUctuating Kascade) used to simulate hadronic cascades, and the graphical-interface object-oriented software called ROOT developed at CERN. One aspect of space radiation analysis for which the Monte Carlo's are particularly suited is the study of secondary radiation produced as albedoes about the structural geometry involved.

The broad goal of simulating space radiation transport in materials science by means of the FLUKA code in conjunction with a ROOT-based interface is reviewed. This research necessarily includes the enhancement of heavy-ion interactions in the code from intermediate energies  $< 3$  GeV/A down to 10 MeV. Above 30 GeV/A the Dual Parton Model (DPM) is used up to air shower energies, although the possible improvement of the DPMJET event generator for energies 3-30 GeV/A is being considered. At present two alternative approaches are being explored, one making use of FLUKA's existing PEANUT model and the other focusing on a modification of the RQMD code. The ROOT interface is being developed in conjunction with the CERN ALICE (A Large Ion Collisions Experiment) software team through an adaptation of their existing AliROOT (ALICE Using ROOT) architecture. As an illustration of the utility of secondary albedo and backscatter analysis, we present results from our current investigation of the ATIC (Advanced Thin Ionization Calorimeter) balloon payload in cosmic-ray astrophysics along with some earlier plots of neutron fluences in the Mir spacecraft. A summary of status and current problems in our investigation is also given.

**Keywords: Monte Carlo, cosmic rays, space radiation, albedoes**

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# COMPARISON OF STRUCTURE AND SEGREGATION IN ALLOYS DIRECTIONALLY SOLIDIFIED IN TERRESTRIAL AND MICROGRAVITY ENVIRONMENTS

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The purpose is to compare the structure and segregation in metallic alloys that are directionally solidified in terrestrial and low gravity environments. Models of dendritic growth rely on diffusional transports of heat and solute in the absence of convection. The models predict primary spacings and tip radii, but thermosolutal convection in terrestrially solidified alloys masks the diffusional processes and can cause macro-segregation. The availability of a microgravity environment would provide the opportunity to effect directional solidification with negligible convection. Based on extensive experiments and finite element simulations, it is very clear that thermosolutal convection strongly affects the growth of dendrites, so much that validation of existing models is impossible. Furthermore, the convection can lead to macro-segregates known as freckles, depending on the alloy and growth conditions. Using hypoeutectic Pb-Sb alloys, we have characterized dendrite spacings, volume fraction of interdendritic liquid, and both macro-segregation and micro-segregation in samples grown in an earth-laboratory. Thus, we are poised to compare the structures obtained to those in samples solidified in a microgravity environment.

During the current year we have been writing code to model the solidification at the microstructural level. The model solves the energy and solute conservations using finite element discretizations. The energy equation is solved in a fixed mesh in which the interface is tracked; the solute conservation equation is solved in an independent mesh that is extremely fine at and near the interface and coarser away from the interface. The latter mesh is regenerated at each time step to accommodate the interface-movement. The model has been tested in a number of scenarios and including the two-dimensional solidification of hypoeutectic Pb-Sb alloys.

We also attempted to measure the diffusivity of Sb in Pb melts because it is needed to validate dendritic growth without convection. Pb-2.2% Sb samples were grown in 1, 2, and 3 mm ID quartz capillaries at 82 K/cm and 0.4  $\mu\text{m/s}$ . Precautions to avoid vibrations and to achieve a rapid quench in pre-cooled He were taken. It was found that ampoule diameters as small as 1 mm cannot eliminate the convection. An alternative method must be sought, therefore, for determining the diffusivity. If it is established that purely diffusive transport cannot be obtained, then there may be a need to effect a diffusivity measurement in space to complement the directional solidification experiments.

**Keywords: solidification, dendrites, micro-segregation, macro-segregation**

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**TRANSIENT INTERFACIAL PHENOMENA IN MISCIBLE POLYMER SYSTEMS (TIPMPS)**

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Almost one hundred years ago Korteweg published a theory of how stresses could be induced in miscible fluids by concentration gradients, causing phenomena that would appear to be the same as with immiscible fluids. Miscible fluids could manifest a “transient” or “effective” interfacial tension (EIT). To this day, there has been no definitive experiment to confirm Korteweg’s model but numerous fascinating and suggestive experiments have been reported. The goal of TIPMPS is to answer the question: Can concentration and temperature gradients in miscible materials induce stresses that cause convection?

In 1954 Cahn and Hilliard published their landmark thermodynamic analysis of diffuse interfaces in immiscible materials based on square gradient theory. Although they used different approaches, their mathematical results are similar to Korteweg’s. Both approaches have a single parameter,  $k$  and involve the square of the concentration gradients. We use the Cahn-Hilliard theory to extract the value of  $k$  for a monomer and its miscible polymer from spinning drop tensiometer experiments and estimate it using the analysis of Naumann for polymer/solvent systems.

An interface between two miscible fluids can best be created via a spatially-selective photopolymerization of dodecyl acrylate with a photoinitiator, which allows the creation of precise and accurate concentration gradients between polymer and monomer. Optical techniques will be used to measure the refractive index variation caused by the resultant temperature and concentration fields.

Three tests are planned:

- 1) A variation in width of the transition zone
- 2) A variation in polymer conversion along a transition zone of constant width
- 3) An imposed temperature gradient along a transition zone of constant width with constant polymer conversion

The convection induced by variations in the interfacial width can be studied independently from that caused by temperature and concentration gradients with a uniform interface width.

We developed a model consisting of the heat and diffusion equations with convective terms and of the Navier-Stokes equations with an additional volume force written in the form of the Korteweg stresses arising from nonlocal interaction in the fluid. The fluid’s viscosity dependence on polymer conversion and temperature was taken from measurements of poly(dodecyl acrylate). Numerical modeling demonstrated that significant flows would arise for conditions corresponding to the planned experiments.

Because the large concentration and temperature gradients cause buoyancy-driven convection that prevents the observation of the predicted flows, the experiment must be done in microgravity.

**Keywords: miscible interface, convection, Korteweg stress, polymer, flight**

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## THE EFFECT OF NANOPARTICLES FILLERS ON DEWETTING DYNAMICS

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Nanoscale metallic particles have been added to polymers for years to significantly enhance various properties such as UV absorption, electrical conductivity, and optical dispersion. In contrast to bulk fillers, which are added in large quantities in order to reinforce structural properties, the concentration of metallic nanoparticles required to affect the electronic response is often less than 5%. Furthermore, since these nanoparticles are coated with surfactants used as dispersants, it has been assumed that they do not interact with the polymer chains, and hence do not affect properties such as viscosity, glass transition, or interfacial tensions. Thus, not much attention has been given to the effect of fillers on thin film stability.

Producing a stable polymer film is a challenge, since dewetting tends to rupture the film. Here, we report on a unique strategy to control the rate of dewetting of thin polymer films by dispersion of various nanoparticle fillers. Specular x-ray reflectivity and TEM are used to profile the distribution of the particles in and out of the plane of the substrate, respectively. Optical microscopy and Lateral force microscopy are used to study the growth rate of holes and position of the particles during the dewetting.

We have carried out systematic dewetting studies of polystyrene (PS) on poly(methyl methacrylate) (PMMA) by adding functionalized fillers like Au and Pd. We show that even in the case where particles are well dispersed, large effects on the stability of the film due to dewetting may be induced by the addition of fillers. The rate of dewetting also depends upon nanoparticle concentration in the film. These results are compared with Molecular Dynamics simulations currently being conducted. As for now, these effects are not theoretically proven, but it is clear that by addition of nanoparticles a combination of equilibrium and kinetic effects can be controlled. Two separate models have been developed to prove the mechanism behind the suppression and expression of the dewetting. The effects presented here promise to be an important means of controlling thin film stability.

**Keywords:** metallic nanoparticles, film stability, dewetting, new research

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## **IMPROVED CRYSTAL QUALITY BY DETACHED SOLIDIFICATION IN MICROGRAVITY**

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Many microgravity directional solidification experiments yielded ingots with portions that grew without contacting the ampoule wall, leading to greatly improved crystallographic perfection. Our long term goals have been:

- To develop a complete understanding of all of the phenomena of detached solidification.
- To make it possible to achieve detached solidification reproducibly.
- To increase crystallographic perfection through detached solidification.

We have three major achievements to report here:

1. We obtained a new material balance solution for the Moving Meniscus Model of detached solidification. This solution greatly clarifies the physics as well as the roles of the parameters in the system.
2. We achieved detached solidification of InSb growing on earth in BN-coated ampoules.
3. We performed an extensive series of experiments on freezing water that showed how to form multiple gas bubbles or tubes on the ampoule wall. However, these did not propagate around the wall and lead to fully detached solidification unless the ampoule wall was extremely rough and non-wetted.

Non-dimensionalization of the governing equations for the Moving Meniscus Model of detached solidification in zero gravity allowed consolidation of the operating conditions and physical properties into five dimensionless parameters. At steady state, the flux of gas dissolved in the melt moving toward the freezing interface must equal the sum of the flux of gas into the gap plus that being incorporated in the growing solid. Both numerical and material balance results give two solutions, with an extremum value of each variable beyond which steady detachment is impossible. This behavior is now understood to originate from satisfaction of the material balance at two different gap widths, with these two solutions becoming identical at an extremum condition beyond which the material balance cannot be satisfied. Only one solution is obtained when no gas is incorporated in the solid. In the presence of gravity, the gas pressure in the gap must be much larger to compensate for the added hydrostatic pressure, causing the gap width to be narrow.

A new method was developed for coating the interior of silica ampoules with boron nitride, which is known to yield low contact angles for semiconductor melts. (A low contact angle favors detached solidification.) Vertical Bridgman solidification of InSb frequently gave portions that were detached, sometimes entirely circling the ingot and sometimes with small facets.

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**Keywords: indium antimonide, detached solidification, dewetting, new research**

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## MEASUREMENTS OF THERMOPHYSICAL PROPERTIES OF MOLTEN SILICON AND GERMANIUM (Ground-based Research Program)

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The electrostatic levitation (ESL) facility at the Jet Propulsion Laboratory was moved to the Materials Science Department of the Caltech campus. Since the move the system up-grades have been made so that more accurate thermophysical properties can be measured.

The most important improvement was in attaining uniform sample temperature. In the previous experiments only one laser beam was used to heat the samples. A simple heat-transfer calculation predicts a large temperature gradient across a sample that becomes even larger as the temperature is raised. Various thermophysical properties that have been measured using single laser beam must have effects that originated from such temperature gradients. Thus one of the major upgrade that has been made in our ESL facility was to design and implement a four-beam heating system that warrants uniform sample temperature.

Density of a high temperature melting material is measured by video imaging the sample in levitation and analyzing the images that are taken over a wide temperature range. However, the density so obtained will be erroneous if the video sensor has blooming effect. An important improvement has been made to reduce such undesirable errors in measured densities by selecting a sensor that is sensitive to the back lit UV while ignoring the thermal radiation from samples. Also developed was a new image analyzing software that can acquire images in real time and accurately analyze them.

Beside these, a numerous improvements have been made to the ESL system: (a) New sample levitation software was developed and implemented based on a faster microcomputer platform. (b) New temperature measurement/analysis software was developed. Along with independently measured spectral emissivity, we should be able to measure true sample temperatures. (c) Development of a method that can accurately measure surface tension and viscosity is in progress. This method utilizes a line scan video camera to detect both the frequencies and the damping constants of oscillating drops. This method is expected to increase accuracy of particularly the viscosity measurements. (d) Developed along with this software is a new laser power control software that remotely controls the laser power that heats the sample.

Using these upgraded ESL system a new attempt will begin to measure various thermophysical properties of molten silicon, germanium, and their alloys.

**Keywords: molten silicon, germanium, ESL, thermophysical properties, characterization**

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**COARSENING OF FACETED CRYSTALS****Gregory S. Rohrer\*, C. Lane Rohrer, and William W. Mullins**

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The conventionally accepted theory for coarsening assumes that crystals grow (or shrink) by the addition (or removal) of atoms that are transported to (or away from) the crystal by capillary-driven diffusion. The assumption that the rates of growth and dissolution are limited by atomic diffusion implies that the surface attachment process is relatively rapid. This assumption seems to be appropriate for crystals with rough surfaces or crystals where the surfaces have step producing defects. However, there is a well known nucleation energy barrier (NEB) for the addition or removal of atoms from an ideal flat facet. The purpose of the present paper is to describe the influence of the NEB on the capillary-driven coarsening of faceted crystals.

Our mean field numerical approach assumes that the particles are fully faceted and this implies that for a crystal to change size while retaining its shape, new layers of atoms must be added to or subtracted from the facets. For this to happen, the crystal must pass through a relatively higher energy state where there is a partial layer (or nucleus) on a facet. Because of this higher energy state, there is a NEB proportional to the crystal size that must be overcome by a thermal fluctuation in order for coarsening to proceed. In general, there are NEB's both for particle growth and particle dissolution. It is the presence of this thermally activated process or fluctuation that distinguishes the coarsening of faceted crystals from that of non-faceted or rough crystals. Therefore, we construct our model with the assumption that two processes must occur in series: diffusion through the medium that supplies and removes material from the crystals and the nucleation events necessary for the advance or retreat of a facet.

The results from our numerical simulations indicate that for perfect crystals, the NEB limits growth when  $R^*$  (the particle size that neither grows nor shrinks) is larger than a few tens of nanometers. When ideal and defect containing crystals coarsen simultaneously, the defective crystals can grow at a rate limited by diffusion and a bimodal grain size is established. The results suggest that when faceted ceramic materials coarsen in a liquid medium, the grains that grow abnormally (much faster than others) are those that contain step producing defects that impinge on the flat facets. Assuming this to be true, it allows us to predict that the number density of abnormal crystals should be roughly constant during growth. Furthermore, the bimodal grain size distribution characteristic of abnormal coarsening should evolve to a normal distribution when all of the perfect crystals have been consumed.

Supported by NASA Microgravity Research Division.

**Keywords: crystal growth, coarsening, nucleation, faceted crystals, new research**

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## SELF-PROPAGATING FRONTAL POLYMERIZATION IN WATER AT AMBIENT PRESSURE

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Water at atmospheric pressure is most convenient solvent to employ and the most important for practical applications (because of the cost and environmental issues associated with DMSO and other solvents). Nevertheless, to our knowledge, steady, self-propagating polymerization fronts have not been reported in water at atmospheric pressure. Currently, polymerization fronts require a high boiling point solvent (either water at high pressures or an alternative solvent such as dimethyl sulfoxide (DMSO) (boiling point 189°C at atmospheric pressure.) Early work on frontal polymerization employed pressures up to 5000 atm in order to avoid boiling of the monomer/solvent/initiator solution. High boiling point solutions are needed because in order to produce a propagating front, a high front temperature is needed to produce sufficiently rapid decomposition of the free radical initiator and subsequent free radical polymerization and heat release at a rate faster than heat losses remove thermal energy from the system.

In this work, frontal polymerization at ambient pressure using water as the solvent is demonstrated using a very reactive monomer (acrylic acid, AA) and free-radical initiator (ammonium persulfate, AP). Only a certain range of AA and AP concentrations produced steadily propagating fronts that neither extinguish due to too low peak temperatures nor bubble violently due to peak temperatures above the solution boiling point. The extinction limit is shown to be due to heat losses to ambient air via buoyant convection. Means to extend the range of bubbling-free, extinction-free conditions are proposed.

In order to study buoyancy-driven instabilities of polymerization fronts, the dynamics of miscible, reacting fluids in a narrow gap (Hele-Shaw cell) were investigated by means of two- and three-dimensional numerical simulations based on the Stokes equations. The kinetics of the chemical front between the two fluids were described by a cubic reaction term in the concentration equation. For low values of the Rayleigh number  $Ra$ , perturbations of the reaction front that are initially antisymmetric across the gap were found to be more unstable than their symmetric counterparts. For larger values of  $Ra$ , on the other hand, simulations show that all forms of initial perturbations eventually lead to strongly symmetrical fingering. The computational simulations are compared with corresponding linear stability results in order to identify the dominant mechanisms driving the instability. Furthermore, comparisons with the experiments of Boeckmann and Mueller, as well as the gap-averaged numerical simulations of DeWit, were conducted to establish the range of validity of the gap-averaging procedure.

**Keywords:** frontal polymerization, free radical polymerization, instability, extinction, acrylic acid, new research

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**SURFACE AND INTERFACIAL STRUCTURES INDUCED BY ELECTROHYDRODYNAMIC INSTABILITIES**

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External electric fields were used to amplify the thermal fluctuations at liquid/air and liquid/liquid interfaces. The electrostatic pressure at the interface operates against the Laplace pressure, given by the product of the interfacial tension and the curvature of the fluctuation, to induce the electrohydrodynamic instabilities. Small wavelength fluctuations are suppressed, since they are too costly energetically. Long wavelength fluctuations, on the other hand, are also suppressed due to the fluid dynamics. Consequently, interfacial fluctuations having a characteristic wavelength  $\lambda_{\text{max}}$  grow, producing structures at the interface having well-defined shapes and separation distances. A simple theoretical framework to describe experimental observations is presented. The theoretical model predicts a substantial reduction in the characteristic wavelength  $\lambda_{\text{max}}$  if the surface energy is replaced by interfacial energy, which occurs when the air is replaced by a second dielectric liquid in the bilayer case. Using reduced variables, a master curve was developed, which quantitatively describes the experimental data for all system studied under different geometries with no adjustable external parameters. Our results show that a submicron structure formation and replication can be easily done.

**Keywords: surface, interface, electrohydrodynamic instabilities**

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# A HYBRID CONSTITUTIVE MODEL FOR PARTICULATE SUSPENSION OF ZEOLITE CRYSTAL GROWTH

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Zeolites are hydrated aluminosilicate materials that are extensively used in the chemical process industry as catalysts, ion exchanger and adsorbents. However, the optimization of zeolite crystal synthesis from particulate suspension remains a technical challenge due to the complexity of underlying mechanisms of phase transition and rheology. Typically, the process involves the formation and dissolution of a gel phase and the nucleation and growth of crystals. The solid fraction can vary over a wide range and the suspension microstructure can be chain-like as occurs during gel formation or globular as a consequence of nucleation during the crystallization process.

A hybrid constitutive model is developed here to represent the thixotropic behavior of the particulate suspension. This model is valid over the complete range of solid fractions typical in the zeolite crystal growth process. Two internal variables, agglomeration and contiguity, are used to describe the degree to which the gel particles and agglomerates form short-range and long-range networks, respectively. The contiguity parameter effectively weighs the effects of hydrodynamic to chain-like network deformation on the viscosity of the suspension. The evolution of microstructure and volume fraction of gel and crystals are described by assuming homogeneous nucleation and surface reaction-controlled crystal growth.

The model predicts the thixotropic behavior of suspension. The effective viscosity rapidly increases as the gel phase forms through polymerization of reagents. As the gel dissolves upon hydrothermal treatment, the long-range connectivity breaks down and in turn the effective viscosity decreases. The nucleation and crystal growth can induce the buildup of solid particle agglomerates through viscoplastic deformation of solid necks and hydrodynamic effect, leading to an increase in the effective viscosity. Complete dissolution of the gel phase again reduces the viscosity. The model predictions compare favorably with a recent set of experimental data on zeolite particulate suspensions.

**Keywords:** zeolite, particulate suspension, rheology

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**NON-INTRUSIVE MEASUREMENT OF THERMOPHYSICAL PROPERTIES OF LIQUIDS  
BY ELECTROSTATIC-ACOUSTIC HYBRID LEVITATION**

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*Thermocapillary flow measurements using acoustically levitated and drastically flattened drops.* The technique involves levitation of a liquid drop and drastically flatten it using acoustic force. The drop is then locally heated by a laser beam, and the fluid flow generated by the local heating is visualized by adding tracer particles. The temperature distribution is also determined by thermography and these measurements will be used to infer the thermal diffusivity and viscosity.

As another approach, flattened drop is heated throughout and then allowed to cool naturally by heat loss from the surface. Due to acoustic streaming, the heat loss mainly occurs through the equator section of the drop. An IR camera aimed on the top surface of the drop records the transient temperature of the drop during the cooling process. The measured cooling rate in combination with a radial heat conduction calculation allows us to determine the thermal diffusivity coefficient of the drop. We have demonstrated the feasibility of the technique using glycerin drops as a model liquid.

*Viscosity determination from the shape relaxation of ultrasonically levitated and initially elongated drops.* The technique involves acoustically spinning and elongating a liquid drop beyond the 2-lobed bifurcation point. Then, the drop is allowed to reverse the elongation process and relaxes (retracts) to its initial shape with a history that depends on the physical properties. We have implemented this novel idea with an acoustic on sucrose solutions to demonstrate the feasibility. Measurements of the time history of two representative dimensions of the elongated drop, the length and the width at the waist, were conducted and an existing relaxation model was used to relate these measurements to the viscosity of the liquid. The obtained viscosity values show a good correlation with those determined by the falling ball method.

*Viscosity determination from the shape relaxation of electrostatically levitated drops.* Using an electrostatic levitator, a liquid drop is levitated and deformed into an oblate shape using acoustic pressure. Then, the drop is allowed to relax to restore the original shape (nearly spherical shape). The time-dependent deformation parameters during the relaxation are correlated to the viscosity through a relaxation model that we have formulated. The comparison of the model with the experimental results reveals an order of difference in the viscosity value, a discrepancy that is being investigated.

**Keywords: non-contact, thermophysical properties, undercooling, levitation.**

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**FROM OXYGEN GENERATION TO METALS PRODUCTION:  
IN SITU RESOURCE UTILIZATION BY MOLTEN OXIDE ELECTROLYSIS**

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For the exploration of other bodies in the solar system, electrochemical processing is arguably the most versatile technology for conversion of local resources into usable commodities: by electrolysis one can, in principle, produce (1) breathable oxygen, (2) silicon for the fabrication of solar cells, (3) various reactive metals for use as electrodes in advanced storage batteries, and (4) structural metals such as steel and aluminum. Even so, to date there has been no sustained effort to develop such processes, in part due to the inadequacy of the database. The objective here is to identify chemistries capable of sustaining molten oxide electrolysis in the cited applications and to examine the behavior of laboratory-scale cells designed to generate oxygen and to produce metal.

The basic research includes the study of the underlying high-temperature physical chemistry of oxide melts representative of lunar regolith and of Martian soil. To move beyond empirical approaches to process development, the thermodynamic and transport properties of oxide melts are being studied to help set the limits of composition and temperature for the processing trials conducted in laboratory-scale electrolysis cells. For optimization, the kinetics of the relevant electrode processes are being studied by a.c. voltammetry and electrochemical impedance spectroscopy. The goal of this investigation is to deliver a working prototype cell that can use lunar regolith and Martian soil to produce breathable oxygen along with metal by-product. Additionally, the process can be generalized to permit adaptation to accommodate different feed-stock chemistries, such as those that will be encountered on other bodies in the solar system.

The expected results of this research include (1) the identification of appropriate electrolyte chemistries; (2) the selection of candidate anode and cathode materials compatible with electrolytes named above; and (3) performance data from a laboratory-scale cell producing oxygen and metal. On the strength of these results it should be possible to assess the technical viability of molten oxide electrolysis for *in situ* resource utilization on the Moon and Mars. In parallel, there may be commercial applications here on earth, such as new “green” technologies for metals extraction and for treatment of hazardous waste, e.g., fixing heavy metals.

**Keywords:** oxygen generation, metal production, *in situ* resource utilization (ISRU), electrolysis

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**LATTICE BOLTZMANN COMPUTATIONS OF BINARY DIFFUSION IN LIQUIDS  
UNDER STOCHASTIC MICROGRAVITY**

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We have conducted research to further develop the Lattice Boltzmann (LB) model in liquids as a computational tool to better understand convective diffusion in stochastic microgravity. We focus on the prototype problem of mathematical modeling of binary liquid alloy diffusion couples in microgravity. Our specific objective is to estimate the accuracy of, or make corrections to, binary liquid diffusivities measured in microgravity. The same methodology should be useful to analyze other experiments in microgravity that involve convective diffusion.

We have reformulated the Lattice Boltzmann model for binary fluids by incorporating three relaxation times, one for interaction of A atoms among themselves, another for interaction of B atoms among themselves, and a third for interaction between A and B atoms. [1] This model enables us to control the magnitude of the chemical diffusivity independent of the viscosity, which was not possible with previous Lattice Boltzmann models. We have performed numerical computations for diffusion in binary liquid diffusion couples in a gravitational field. These were done for two interpenetrating ideal gases having atoms of differing mass. We observe interdiffusion profiles as well as gravitational settling. Since the Rayleigh number for a gas is inversely proportional to its diffusivity, we use an artificially high gravity to simulate interdiffusion in liquids, which have a much smaller diffusivity than gases. We have also shown that various finite difference schemes used to solve the LB equations lead to different apparent viscosities. [2] These apparent viscosities are the sum of a physical viscosity (the true viscosity) and a specious numerical viscosity (a false viscosity that depends on the computational scheme and parameters such as spatial and temporal grid sizes). By means of analysis of the finite difference equations, we have worked out formulae for these specious numerical viscosities and have performed numerical LB simulations that verify these results. We have used the LB model to investigate the no-slip boundary condition for Poiseuille flow in a channel. We study this problem as a function of the Knudsen number, which is the ratio of the mean free path to the system size. For small Knudsen number, LB simulations yield the classical parabolic velocity profile characteristic of the no-slip condition. But for large Knudsen number, the LB simulations yield a flat profile more nearly characteristic of “plug flow” and the no-slip boundary condition is violated. This is in agreement with the general expectation that for large Knudsen number, the mean free path is sufficiently large compared to the system size that the molecules do not “see” the walls of the container locally. These results need further study and could be important for aerodynamics.

[1] Sofonea, V. and Sekerka, R. F. “BGK models for diffusion in isothermal binary fluid systems,” *Physica A* 299 494-520 (2001)

[2] Sofonea, V., and Sekerka, R. F. “Viscosity of Finite Difference Lattice Boltzmann Models,” submitted to *J. Computational Physics*

**Keyword: theoretical**

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# INFLUENCE OF PROCESSING CONDITIONS ON THE LOW TEMPERATURE PROPERTIES OF GLASSES

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The low temperature properties of glasses differ significantly from their crystalline counterparts due to the presence of a broad distribution of two level systems (TLS). These excitations affect a variety of physical properties ranging from specific heat and thermal conductivity to mm-wave absorption and Raman scattering. Since laboratory studies of such TLS excitations in amorphous silicate dust grains indicate that they dominate the mm and submillimeter wave temperature dependent properties in the temperature range appropriate to interstellar dust emission, there is broad interest in identifying the source of these excitations. Despite the outstanding success of the phenomenological tunneling model, it does not answer fundamental questions such as how these TLS result from the microscopic properties of the glass.

In order to examine the dependence of TLS on defects and glass homogeneity we have constructed a gas film levitation (GFL) furnace system for controlled glass sample processing. The central component is the evacuable water-cooled furnace container, which holds the graphite heater element and the graphite crucible. An IR emission method is used to monitor thermal events in the melt, such as the glass transition and crystallization. In this GFL furnace, a regulated flow of Ar gas diffuses through the porous graphite crucible so that the resulting gas layer isolates the melt from the crucible surface. Because contact with the crucible walls is reduced, heterogeneous nucleation of crystallites is suppressed, making possible very low cooling rates and higher quality glass than can be achieved by conventional methods.

So far two different kinds of samples have been processed with the GFL system: a ZBLAN fluoride glass and a soda-lime silica glass. Our first measurements have focused on the temperature dependent part of the mm-wave absorption spectrum in the region  $2 - 20 \text{ cm}^{-1}$  (5 mm to 0.5 mm wavelength) at temperatures of 1.2 – 10 K, which is dominated by resonant TLS absorption. The results are quite interesting. For the ZBLAN fluoride glass which has a high fragility (strongly non-Arrhenius temperature dependence of the relaxation time in the melt) the TLS spectrum is independent of processing, while for the less fragile soda-lime silica glass (more Arrhenius-like temperature dependence of the relaxation time) the TLS absorption spectrum is reduced significantly ( $\sim 50\%$ ) in the low frequency ( $2\text{-}5 \text{ cm}^{-1}$ ) region. Raman spectroscopic measurements are planned since they provide information on the quality of the resulting glass network as well as additional information on the TLS related dynamics and also on the ubiquitous, higher frequency Boson peak.

**Keywords:** glasses, TLS, low temperature anomalies, fragility, levitation, new research

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## **UNDERCOOLING OF FERROMAGNETIC MELTS**

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We have studied the undercooling of Pd-Co melts below their ferromagnetic Curie points. We have developed a model for including the magnetic contribution to the energy of formation of the alloy crystal nucleus from a liquid alloy of a different composition. The results are in good agreement with the measured composition dependence of the maximum attainable undercooling.

**Keywords:** undercooling, Pd-Co, ferromagnetic, alloy, new research

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**DYNAMIC BIAxIAL FLEXURAL STRENGTH OF THIN CERAMIC SUBSTRATES****Ming Cheng, Weinong Chen, and K.R. Sridhar\***

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Ceramic membranes are used as molecular filters in fuel cells and solid oxide electrolyzers for oxygen generation in space exploration missions. Development of high-reliability substrate materials inevitably requires the accurate characterization of the mechanical properties of those materials that have superior potential in their physical and electrical properties. Unfortunately, there is a lack of experimental techniques that can provide such critical data for thin and brittle sheets of materials. In this paper, a dynamic piston-on-3-ball experimental technique is developed for a biaxial flexural strength test of thin ceramic substrates at high loading rates. In order to maintain the same experimental conditions, except for the loading rates, the test section of the new dynamic piston-on-3-ball experimental facility is identical to the test section of the ASTM standard quasi-static piston-on-3-ball setup, making the high loading rate results directly comparable to the standard quasi-static results. Analytical modeling of this technique guides the experimental design and is used to judge the validity of experimental results. The upper and lower limits of the loading-rate range for a valid experiment with a specific specimen are then analyzed. Thin ceramic substrates made of pure 8-mol% yttria stabilized zirconia (8YSZ) as well as its doped versions are tested using this experimental technique, as well as its standard counterpart—the quasi-static piston-on-3-ball technique. Results show that the mean biaxial flexural strength increases with loading stress-rate.

A material model is necessary to obtain an insight into the dynamic strength behavior of ceramic materials. Although material models have been proposed to describe the dynamic constitutive behavior of brittle materials under constant strain-rate loading conditions, few efforts were found to explain such dynamic behavior under constant stress-rate loading, which is the loading condition for many dynamic experimental techniques, such as this new dynamic piston-on-3-ball experimental technique, and is significant in practical use. In this paper, a new model for dynamic strength under constant stress-rate loading for brittle materials is developed based on the concept of cumulative damage. The parameters in this model can be experimentally identified using an overall least squares curve-fitting technique for all the data at different loading stress-rates, thus avoiding the massive requirements on experimental data that are neither economical nor practical to obtain. Experimental results on pure and doped ceramic material 8YSZ thin sheets are used to determine the constants in this new model. The model is found to give a good description of the dynamic constitutive behavior of brittle thin sheets under biaxial bending.

**Keywords:** biaxial, strength, dynamic, ceramic, stress-rate, ISRU

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## PARTICLE ENGULFMENT AND PUSHING BY SOLIDIFYING INTERFACES

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The study of particle behavior at solid/liquid interfaces (SLI's) is at the center of the *Particle Engulfment and Pushing* (PEP) research program. Interactions of particles with SLI's have been of interest since the 1960's, starting with geological observations, i.e., frost heaving. Ever since, this field of research has evolved as being significant to metal matrix composite materials, fabrication of superconductors, inclusion control in steels, and many other fields. The PEP research effort is geared to understand the fundamental physics of the interaction between particles and a planar SLI. Experimental work including 1-g and  $\mu$ -g experiments accompany the development of analytical and numerical models.

The experimental work comprised of substantial groundwork with aluminum and zinc matrices containing spherical zirconia particles,  $\mu$ -g experiments with metallic Al matrices and the use of transparent organic metal-analogue materials.

The impetus of the first  $\mu$ -g experiment with metallic matrices was the proof of concept and technical feasibility. The second  $\mu$ -g experiments with organic materials yielded a substantial database for the evaluation of PEP models. Current efforts are geared towards the development of suitable ampoules for planned experiments on board the International Space Station, in conjunction with verification of the thermal requirements of the furnace module. In addition, real-time X-ray studies of SLI interaction with a second phase, i.e., gas pores and insoluble particles, are used to investigate the influence of the thermal and solutal field on the SLI morphology and the subsequent effect on the critical velocity of engulfment.

The modeling efforts have grown from the initial steady-state analytical model to dynamic models, accounting for the initial acceleration of a particle at rest by an advancing SLI. To gain a more comprehensive understanding, numerical models were developed to account for the influence of the thermal and solutal field, on the critical velocity of engulfment. In addition, theoretical calculations using FIDAP software were performed to determine the relative effect of the different forces acting on a particle as a function of the gravity level and the orientation of the gravity vector with respect to the growth direction. Current efforts are geared towards the numerical calculation of the drag force and to couple the diffusive 2-D front tracking model with a fluid flow model to account for differences in the critical velocity of engulfment in 1-g and  $\mu$ -g environments.

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**Keywords:** particle pushing, interface tracking, interface morphology,  $\mu$ -g experiments

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## CRYSTAL GROWTH OF ZnSe AND RELATED TERNARY COMPOUND SEMICONDUCTORS BY VAPOR TRANSPORT

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The objective of the project is to determine the relative contributions of gravity-driven fluid flows to the compositional distribution, incorporation of impurities and defects, and deviation from stoichiometry observed in the crystals grown by vapor transport as results of buoyance-driven convection and growth interface fluctuations caused by irregular fluid-flows. ZnSe and related ternary compounds, such as ZnSeS and ZnSeTe, were grown by vapor transport technique with real time in-situ non-invasive monitoring techniques. The grown crystals were characterized extensively to correlate the grown crystal properties with the growth conditions.

The following is the research progress in the past two years. In-situ monitoring of partial pressure by optical absorption technique and visual observation of the growing crystal were performed during vapor growth of ZnSe. Low-temperature photoluminescence (PL) spectra and glow discharge mass spectroscopy (GDMS) were measured on ZnSe starting materials provided by various vendors and on bulk crystals grown from these starting materials by physical vapor transport (PVT) to study the effects of purification and contamination during crystal growth process. Optical characterization was performed on wafers sliced from the grown crystals of ZnSe, ZnTe and  $\text{ZnSe}_{1-x}\text{Te}_x$  ( $0 < x < 0.4$ ). Energy band gaps at room temperature were determined from optical transmission measurements and a best fit curve to the band gap vs. composition,  $x$ , data gives a bowing parameter of 1.45. Low-temperature photoluminescence (PL) spectra of ZnSe and ZnTe were dominated by near band edge emissions and no deep donor-acceptor pairs were observed. The PL spectrum exhibited a broad emission for the  $\text{ZnSe}_{1-x}\text{Te}_x$  samples,  $0.09 < x < 0.39$ . The single broad PL emission spectra and the spectra measured as a function of temperature were interpreted as being associated with the exciton bound to Te clusters because of the high Te content in these samples. To validate numerical codes, in-situ monitoring during the PVT of  $\text{HgI}_2$  was designed. Optical absorption spectra of the vapor phase over  $\text{HgI}_2(\text{s,l})$  were measured for wavelengths between 200 and 600nm at sample temperatures between 349 and 610K. The Beer's Law constants for 15 wavelengths between 200 and 440 nm were determined. From these constants the vapor pressure of  $\text{HgI}_2$  was established as a function of temperature for the liquid and the solid  $\beta$ -phases. To characterize the growth conditions during the PVT growth of In-doped ZnSe the optical absorbance of the vapor phase over the In-Se system were measured and were used to obtain the partial pressures of  $\text{Se}_2(\text{g})$  and  $\text{In}_2\text{Se}(\text{g})$ .

**Keywords:** physical vapor transport, ZnSe, ZnSeTe, flight

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**STRUCTURAL FLUCTUATIONS AND THERMOPHYSICAL PROPERTIES OF  
MOLTEN II-VI COMPOUNDS**

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The objectives of the project are to conduct ground-based experimental and theoretical research on the structural fluctuations and thermophysical properties of molten II-VI compounds to enhance the basic understanding of the existing flight experiments in microgravity materials science programs as well as to study the fundamental heterophase fluctuation phenomena in these melts by:

- 1) conducting neutron scattering analysis and measuring quantitatively the relevant thermophysical properties of the II-VI melts (such as viscosity, electrical conductivity, thermal diffusivity and density) as well as the relaxation characteristics of these properties to advance the understanding of the structural properties and the relaxation phenomena in these melts and
- 2) performing theoretical analyses on the melt systems to interpret the experimental results.

All the facilities required for the experimental measurements have been procured, installed and tested. Thermal diffusivity of molten tellurium has been measured by a laser flash method in the temperature range of 500 °C to 900 °C. The measured diffusivity as a function of temperature agrees fairly well with published data. However, a relaxation phenomenon, which shows a slow drift of the measured thermal conductivity toward the equilibrium value after cooling of the melt, was observed for the first time. An apparatus based on the transient torque induced by a rotating magnetic field has been developed to determine the viscosity and electrical conductivity of semiconducting liquids. Viscosity measurements on molten tellurium showed a similar relaxation behavior to the measured diffusivity. The density and volume expansion coefficients for pure Te and HgTe melts were measured as a function of temperature using a pycnometric method. A density maximum was found for both melts but no relaxation behavior was observed. Neutron scattering experiments were performed on the HgTe and HgZnTe melts and the results on pair distribution showed better resolution than previously reported. A simple kinetic theory, which contains the formation reactions of Te polymerization that increases the molecular weight, was proposed to interpret the relaxation behavior of HgZnTe viscosity data.

**Keywords: thermophysical and thermodynamic properties, II-VI compounds**

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## REDUCTION OF DEFECTS IN GERMANIUM-SILICON (RDGS)

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Crystals grown without contact with a container have far superior quality to otherwise similar crystals grown in direct contact with a container. In addition to float-zone processing, detached-Bridgman growth is a promising tool to improve crystal quality, without the limitations of float zoning. Goals of this project include the development of the detached Bridgman process to be reproducible and well understood and to quantitatively compare the defect and impurity levels in crystals grown by these three methods.

Earth based experiments on the science of detached crystal growth are being conducted on germanium and germanium-silicon alloys in preparation for a series of experiments aboard the International Space Station. The purpose of the microgravity experiments includes differentiating among proposed mechanisms of detachment, and confirming or refining our understanding of detachment. Because the contact angle is critical to determining the conditions for detachment, the sessile drop method was used to measure the contact angles as a function of temperature and composition for a large number of substrates made of potential ampoule materials. Growth experiments have used pyrolytic boron nitride (pBN) and fused silica ampoules with the majority of the detached results occurring predictably in the pBN. The nature and extent of detachment is determined by using profilometry in conjunction with optical and electron microscopy. The stability of detachment has been analyzed, and an empirical model for the conditions necessary to achieve sufficient stability to maintain detached growth for extended periods has been developed. Results in this presentation will show that we have established the effects on detachment of ampoule material, pressure difference above and below the melt, and silicon concentration; samples that are nearly completely detached can be grown repeatedly in pBN.

Etch pit density (EPD) measurements of normal and detached Bridgman-grown Ge samples show a two order of magnitude improvement from growing detached. Comparison of normal Bridgman and float-zone samples of GeSi alloys up to 10 at% Si show the float-zone samples have an order of magnitude lower EPD. Detailed comparisons will be presented.

**Keywords: detached Bridgman growth, crystal growth, germanium, germanium-silicon**

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**THE FEATURES OF SELF-ASSEMBLING ORGANIC BILAYERS IMPORTANT  
TO THE FORMATION OF ANISOTROPIC INORGANIC MATERIALS  
IN MICROGRAVITY CONDITIONS**

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There is a growing need for anisotropic inorganic particles in a variety of materials science applications. Structural, optical, and electrical properties can be greatly augmented by the fabrication of composite materials with anisotropic microstructures or with anisotropic particles uniformly dispersed in an isotropic matrix. Examples include structural composites, magnetic and optical recording media, photographic film, certain metal and ceramic alloys, and display technologies including flat panel displays. While there has been considerable progress toward developing an understanding of the synthesis of powders composed of monodispersed, spherical particles, these efforts have not been transferred to the synthesis of anisotropic nanoparticles. This project explores the use of anisotropic micellar structures to template anisotropic particles in both metallic and inorganic salt systems. Examples of anisotropic particles formed to date include platelet particles of the metals Pt, Au, and Ag, and the semiconductor CdS, each prepared using organic lamellar templates.

We have observed that there are at least two general mechanisms that lead to the templating of two different classes of platelike particles. Each mechanism takes advantage of the processes of confinement, specific interactions and mass transport. The first we will call *crystal templating*, where the products are anisotropic single crystal particles. These particles result from a slow nucleation event, giving relatively few nuclei, and subsequent growth of the individual crystals. The second mechanism we will call *aggregate templating*. Here, the products are assemblies of smaller single crystal particles that aggregate in the shape of a platelet.

While working on particle syntheses associated with this project, we recently discovered that certain classes of mixed organic/inorganic layered solids exhibit liquid crystalline properties. Previously, there were a handful of “mineral liquid crystals” known, and ours are among the first organic/inorganic phases. The principles behind particle-based liquid crystal behavior are similar to molecule- or polymer-based systems, except that the “mesogen” is now an anisotropic particle, such as the platelets we are developing. Some details of these new mineral liquid crystal systems will be presented.

**Keywords: semiconductors, metals, particles, anisotropic particles, new research**

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**SURFACE TENSION AND VISCOSITY OF SCN AND SCN-ACETONE ALLOYS  
AT MELTING POINTS AND HIGHER TEMPERATURES USING  
SURFACE LIGHT SCATTERING SPECTROMETER**

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Succinonitrile has been and is being used extensively in NASA's Microgravity Materials Science and Fluid Physics programs and as well as in several ground-based and microgravity studies including the Isothermal Dendritic Growth Experiment (IDGE). Succinonitrile (SCN) is useful as a model for the study of metal solidification, although it is an organic material, it has a BCC crystal structure and solidifies dendritically like a metal. It is also transparent and has a low melting point (58.08°C). Previous measurements of succinonitrile (SCN) and alloys of succinonitrile and acetone surface tensions are extremely limited. Using the Surface Light Scattering technique we have determined non invasively, the surface tension and viscosity of SCN and SCN-Acetone Alloys at different temperatures.

This relatively new and unique technique has several advantages over the classical methods such as, it is non invasive, has good accuracy and measures the surface tension and viscosity simultaneously. The accuracy of interfacial energy values obtained from this technique is better than 2% and viscosity about 10 %. Succinonitrile and succinonitrile-acetone alloys are well-established model materials with several essential physical properties accurately known - except the liquid/vapor surface tension at different elevated temperatures. We will be presenting the experimentally determined liquid/vapor surface energy and liquid viscosity of succinonitrile and succinonitrile-acetone alloys in the temperature range from their melting point to around 100°C using this non-invasive technique. We will also discuss about the measurement technique and new developments of the Surface Light Scattering Spectrometer.

**Keywords: interfacial energy, succinonitrile, surface light scattering spectroscopy, surface tension, viscosity, characterization**

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**DEVELOPMENT OF A MONTE CARLO RADIATION TRANSPORT CODE SYSTEM FOR  
HEDS: STATUS UPDATE**

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Galactic cosmic rays (GCR) and occasional, but intense, fluxes of solar energetic particles (SEP) present severe radiation hazards to manned planetary exploration. The uncertainties associated with estimating crew radiation risk for these missions are thought to be substantial. The major uncertainty is related to the biological response to high-energy heavy ions in the GCR environment, but a significant uncertainty component is also due to existing radiation transport models and methods used to predict secondary particle fluxes and their spectra behind shielding. Our approach is to develop a radiation transport code system based on Monte Carlo methods, the methodology most commonly used in a variety of technical areas for high-energy radiation transport, but one which has not been previously applied in addressing these space radiation issues. This method has inherent capabilities - namely, 3-D transport, modular programming, and detailed output - that are very important for human exploration and development of space (HEDS) applications. The code used in this work is the High Energy Transport Code (HETC). A major part of the work involves extending HETC to transport the heavy-ion component of the GCR environment. This will be accomplished by incorporating into HETC heavy-ion nuclear collisions models capable of describing the production of all secondary charged and neutral particles produced in the collisions. This new heavy-ion/nucleon-meson transport code, HETC/HEDS, will be coupled with other transport codes specialized for low-energy neutron transport (MORSE) and electron-photon transport (EGS) to provide a full-capability Monte Carlo radiation transport "code system" for HEDS applications.

Modifications of HETC are underway to extend the code to include transport of energetic heavy ions. Those completed or nearly completed include: 1) The range energy tables for all nuclides have been incorporated and debugging processes have started; 2) The interfaces with the cross sections and collision models have been defined and programmed into the heavy ion transport system; 3) The geometry module has been interfaced with the heavy ion transport module. Note that the interfaces mentioned in 2) still require the appropriate collision models/data as inputs. For the latter, a model and associated database for total nuclear cross sections (sum of elastic and inelastic/breakup processes) have been completed. The NUCFRG2 nuclear fragmentation model developed at NASA Langley is being used in conjunction with a momentum distribution model developed at the Naval Research Laboratory to generate the database of secondary charged particles. Progress in model/database development will be reported.

**Keywords: space radiation, shielding, radiation transport, Monte Carlo, nuclear**

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## INTERFACE PATTERN SELECTION CRITERION FOR CELLULAR STRUCTURES IN DIRECTIONAL SOLIDIFICATION (IPSIDS)

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The central focus of this flight-definition investigation is to establish key scientific concepts that govern the selection of interface patterns during the directional solidification of alloys. The critical scientific concepts in the selection of interface patterns will be addressed first, and then the results of ground-based experimental studies in the Al-4.0 wt % Cu system will be presented.

For directional solidification, the key problem is to establish the criteria that dictate the selection of a unique solution, or a certain narrow set of solutions, for cellular and dendritic patterns. In addition, a physical insight into the reason for the multiple solutions is required. The results of a phase field model will be described, and an analytical model will be presented that predicts that the variation in primary spacing in an array is strongly coupled with the variations in tip radius, length of the cell and the width parameter of the cell, and all these four microstructural scales are governed by a unique relationship. We shall then show that ground-based experiments on the three-dimensional patterns show significant disorder in the patterns due to the presence of gravity induced fluid flow, so that low gravity experiments are needed to obtain benchmark data in which gravity-induced fluid flow is negligible. The results of the theoretical model, and the parameters to be measured for low gravity experimental data, will be discussed to obtain quantitative understanding of the fundamental physics of pattern formation and to establish a reliable theoretical framework for the prediction of pattern formation.

The ground-based results to establish the experimental matrix, to determine the physical constants of the system, and to analyze low gravity data will be presented. The experimental matrix was determined by developing a new technique in which diffusive growth could be obtained in very thin samples, i.e. <1 mm diameter for the Al-4.0 wt %Cu alloys. The results of the measurements of two critical system parameters, the interface energy anisotropy and the diffusion coefficient in the liquid, will be presented. We obtained the value of the anisotropy parameter as  $0.098 \pm 0.0008$  with 95% confidence interval in an Al-4.0 wt% alloy, and this the first experimental value for nearly isotropic metallic systems. We shall also show that the diffusion coefficient data reported in the literature are influenced by fluid flow, and the diffusion coefficient was found to be  $2 \times 10^{-9}$  m<sup>2</sup>/s, which is 50% lower than the value reported in the literature. In addition, to analyze the low gravity data, the effect of quenching on the interface shape was determined, and the technique of reconstruction of the three dimensional shape of the array was developed to establish the precision required to obtain reliable values of cell tip radius and cell shape.

**Keywords:** interface patterns, cells, dendrites, directional solidification, phase field, flight

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**DYNAMICAL SELECTION OF THREE DIMENSIONAL INTERFACE PATTERNS  
IN DIRECTIONAL SOLIDIFICATION (DSIP)**

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This investigation is aimed at establishing key scientific concepts that are important in the dynamical selection of interface patterns during the directional solidification of alloys. As the growth velocity is increased, the interface undergoes planar to cellular and cellular to dendritic transitions. These transitions occur under dynamical growth conditions, which requires precise in situ observation of interface patterns. In addition, the unstable planar interface reorganizes into an array of cells and dendrite with some characteristic microstructure whose selection occurs under nonlinear growth condition, which is time-dependent. The aim of this project is to obtain benchmark data required for establishing the detailed dynamics of interface pattern formation in bulk samples and the prediction of the final steady-state pattern..

Two sets of studies will be described: one on the steady-state patterns and the other on the dynamical evolution of the patterns. Experimental studies and the results of the phase field model will be described. Several important results, obtained in the ground-based study, will be described. (1) The microstructural transition from cells to dendrite is not sharp, but a regime of mixed cells and dendrite is present. (2) In the cellular regime, although the shape of the cell and the spacing between the cells in an array show significant variations, a scaling law is observed when all the cell shapes are scaled to the local primary spacing. (3) It is found that the Saffman Taylor shape of viscous fingers could describe the shape of the cells at the advancing front. (4) When an intercellular eutectic is present, the Saffman Taylor finger solution, after slight modification is made to account for the three-dimensionality of cells compared to the two-dimensional fingers, can accurately describe the cell shape. (5) The cell-dendrite transition is found to depend on the local spacing between the cells, and a critical range of  $G/V$  is established in which both cells and dendrites coexist. Furthermore, within this range a critical local spacing is found above which a cell transforms to a dendrite. This critical spacing is found to be given by the geometrical mean of the thermal, solutal and capillary lengths, and inversely proportional to the dimensionless composition in wt. Percent.

A new experimental design of the thermal assembly will be described that will give a planar solid-liquid interface, and ground-based experiments in succinonitrile-salol system will be presented. Experimental observations and the phase field calculations on the dynamics of pattern evolution in two and in three dimensions will be shown through several small digital movies and videos. These videos will also demonstrate the effect of fluid flow on pattern evolution in bulk samples of 1 cm diameter.

**Key words: pattern formation, cells, dendrites, viscous finger, flight**

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# SMALL PARTICLE RESPONSE TO FLUID MOTION USING TETHERED PARTICLES TO SIMULATE MICROGRAVITY

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This paper reports on ground based work conducted to support the Spaceflight Definition project SHIVA (Spaceflight Holography Investigation in a Virtual Apparatus). SHIVA will advance our understanding of the movement of a particle in a fluid. Gravity usually dominates the equations of motion, but in microgravity as well as on earth other terms can become important. Before two members of our team found an analytical solution of the equations, numerical methods and/or neglecting terms were required. The general solution predicts that the usually neglected history term becomes important when the characteristic viscous time is in the same order as the vibration period and peaks when the two times are equal. In this case three force terms, the Stokes drag, the added mass, and the history drag must all be included in predicting particle movement. We also developed diagnostic recording methods using holography to save all of the particle field data, allowing the experiment to essentially be transferred from space back to earth in what we call the “virtual apparatus”. Using state-of-the-art methods in holography we will quantify the three-dimensional motion of sets of particles, allowing us to test and apply the new analytical solutions.

The motion of particles up to 4 mm in diameter in a fluid that oscillates at frequencies up to 100 Hz with amplitudes up to 200 microns is being examined. Ground studies to support the flight development program have employed various schemes to simulate microgravity. One of the most reliable and meaningful methods uses spheres tethered to a fine hair suspended in the fluid. We have also investigated particles with nearly neutral buoyancy. Recordings are made at the peak amplitudes of vibration of the cell providing a measure of the ratio of fluid to particle amplitude. The experiment requires precise location of the particle at the time of recording. The hologram of the particle provides microscopic images of the particle that are used for finding the position with an accuracy of a few microns. To make the experiment more versatile, the spaceflight system will record holograms both on film and electronically. The electronic holograms can be downlinked providing real time data.

Results of the ground experiments, the flight experiment design, and data analysis procedures are reported.

**Keywords:** particle dynamics, Stokes flow, holography, flight

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## USE OF ORGANIC STRUCTURE DIRECTING AGENTS TO CONTROL THE MORPHOLOGY OF ZEOLITE CRYSTALS

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Zeolites are crystalline, microporous, aluminosilicates, that, grown as films, can be used as membranes that offer novel opportunities for applications in membrane reactors, as selective chemical sensors, and in electronic and thermoelectric applications. In order to prepare films with desirable microstructure it is crucial to understand their nucleation and growth mechanisms and develop methods to manipulate their crystal habit. Our work attempts to understand aspects of the mechanisms that govern the crystal growth process of a representative pure silica molecular sieve, silicalite-1 (structure type MFI), and alter these mechanisms at the molecular level to produce the desired crystal shape.

Silicalite-1 crystals are synthesized under hydrothermal conditions from alkaline aqueous solutions. Tetrapropylammonium hydroxide (TPAOH) is typically used in the synthesis of MFI and acts as a structure-directing agent (SDA) or an aid in the formation of its molecular structure. The characteristic MFI crystal shape, using TPAOH, is that of a coffin shape. The zeolite pore structure varies along the different crystallographic axes. Sinusoidal channels (a-axis) are interconnected with straight channels (b-axis) with dimensions ( $\sim 5\text{-}6\text{ \AA}$ ) near the size of many industrially important molecules. Tortuous channels are present along the c-axis, the longest axis of the crystal. Our studies on the growth of MFI crystals show that variation of synthesis conditions leads to slight variations of the coffin shape. The fundamental shape of the crystal remains the same, and the order of the size of the crystal dimensions is also constant ( $c > a > b$ ). These findings are consistent with reported results by other groups.

Syntheses of silicalite-1 membranes using TPAOH show that the crystals are preferentially oriented with their c-axis nearly perpendicular to the substrate. Although our group and others have demonstrated separations using these membranes, the observed fluxes are low for commercial use. A desirable configuration for a selective membrane would be thin and b-oriented. This will allow for the molecular sieving to occur along the straight channels, offering the possibility of increased flux. Our previous studies show that to obtain a membrane with such an orientation we must identify conditions leading to fast growth along the b-axis. However, the single crystal growth studies indicate that synthesis with TPAOH will likely not achieve this.

The use of different SDAs has been therefore explored for the growth of MFI crystals of different crystal shapes. For the first time since its discovery in the 1970's, we have been able to drastically affect the MFI crystal shape and accelerate growth along the b-axis. The effect of this newly observed shape on the membrane growth and microstructure will also be presented along with further insights on the growth mechanisms involved in the evolution of the crystal shape.

**Keywords:** silicalite-1, templates, crystal morphology, membranes, zeolites, new research

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## **COARSENING IN SOLID-LIQUID MIXTURES: A COMPARISON BETWEEN THEORY AND EXPERIMENT**

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Coarsening is a process that occurs in a variety of two-phase mixtures ranging from raindrops in clouds to precipitates in jet turbine blades. During the coarsening process large particles grow at the expense of small particles. This leads to an increase in the average particle size in the system and a change in the properties of the material in many commercial alloys.

Unfortunately, a careful test of these theories, many of which have been in existence since the early 60's, has never been performed. A two-phase mixture composed of solid Sn-rich particles in a Pb-Sn eutectic liquid is an ideal system in which to measure the coarsening kinetics of a two-phase mixture. The solid particles are spherical and, since the thermophysical parameters are known, the results of the experiments can be compared directly to theory with no adjustable constants. To avoid gravitationally induced sedimentation, the experiments were performed on the Space Shuttle during the MSL-1 missions. A careful examination of both the scaled particle size distributions and scaled spatial correlation functions showed that they evolve in time, and thus the system was not in the steady state coarsening regime where most theories are applicable. We therefore compared the experimental results to a theory for nonsteady state coarsening. The theoretically predicted evolution of the particle size distributions and spatial correlation functions agree with the experimental results. Since we find agreement between a theory for transient Ostwald ripening and the experimental results, and disagreement between the experimental results and theories for steady state coarsening, we conclude that steady state theories may have limited applicability for many systems. Nevertheless, the transient calculations show that with still longer coarsening times it may be possible to access the steady-state coarsening regime and test these many theories. To that end, experiments as long as 48 hours are planned for the International Space Station (ISS). The experiments will be performed in the Microgravity Science Glovebox using furnaces developed by the Coarsening in Solid-Liquid Mixtures-II team at NASA Glenn Research Center and Zin Technologies. A presentation of the results from the first spaceflight experiments and our plans for the future experiments on the ISS will be given.

**Keywords: coarsening, Ostwald ripening, solid-liquid mixtures, flight**

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**MODELS TO OPTIMIZE THE BENEFITS OF STEADY AND ROTATING  
MAGNETIC FIELDS FOR CRYSTAL GROWTH IN MICROGRAVITY**

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We have numerically modeled the growth of semiconductor crystals in microgravity by the floating-zone and detached Bridgman processes. For the floating-zone process, we have focused on the stabilization of the thermocapillary and solutocapillary convections with both steady axial magnetic fields and rotating magnetic fields (RMF). Previous linear stability analyses for the floating-zone process with a steady axial magnetic field have only yielded accurate results for very weak magnetic fields because of numerical resolution problems. We have developed a hybrid method which combines analytical solutions for the Hartmann layers adjacent to the liquid-solid interfaces and numerical solutions for the rest of the melt. This hybrid approach yields accurate results for all magnetic field strengths of interest for both terrestrial and microgravity crystal growth. For the floating-zone process, a moderate strength RMF introduces angular momentum which dramatically reduces the magnitude of the thermocapillary and solutocapillary convection and thus stabilizes the melt motion. However at some strength, the RMF produces its own instability. Modeling reveals the optimum RMF for each floating-zone process.

For the detached Bridgman process, an RMF can lead to a more homogeneous crystal and a more planar crystal-melt interface, but again it can lead to its own instability leading to striations in the crystal. Previous treatments of the RMF instability have focused on a uniform density liquid in a closed cylinder. For the detached Bridgman process in microgravity, there is a free surface whose presence dramatically decreases the value of the critical Taylor number at which the RMF instability occurs. In addition, during the detached Bridgman growth of alloyed crystals, such as GeSi, the axial density variation due to the rejection of the heavier species at the crystal-melt interface changes the value of the critical Taylor number at which the RMF instability occurs. The effects of the RMF on the transport of gases which are rejected at the crystal-melt interface has also been modeled since the rate of evaporation of these gases at the periphery of the interface affects detachment.

**Keywords: modeling, magnetic fields, instability, theoretical**

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**PROCESS-PROPERTY-STRUCTURE RELATIONSHIPS IN COMPLEX OXIDE MELTS****Richard Weber\* and Paul Nordine**

Containerless Research, Inc., Evanston, IL

This project is a fairly broad-based investigation of the behavior of molten oxide materials under highly non-equilibrium conditions which can be accessed using containerless techniques. The work is exploring new directions in materials processing which show promise for development of low gravity experiments requiring pristine liquids surfaces and quiescent liquids to decouple convective and diffusive transport. Emphasis is being placed on investigation of alumina-based materials and it includes substituting nitrogen for part of the oxygen in the liquids, determining glass forming behavior and the measurements of the structure of the glasses and liquids. Experiments are being performed at CRI and in collaboration with scientists at NASA and NASDA to establish requirements for glass formation and evaluate measurements of liquid properties, in particular the melt viscosity, using levitation techniques. Additional collaborations with scientists at Argonne National Laboratory, University of California-Davis and the Food and Drug Administration are providing important information about the structure and properties of the new materials which are resulting from this research.

Major accomplishments during the last year were:

1. Construction and testing of a high pressure aerodynamic levitator for investigation of oxynitride liquids at pressures up to 4 bar.
2. Synthesis of oxide and oxynitride glasses.
3. Characterization of the glasses using NMR and thermal analysis.
3. Establishing conditions for electrostatic levitation of oxide liquids.
4. Investigation of the structure of oxide liquids using neutron diffraction in collaboration with scientists at Argonne National Laboratory.

Results of the research will be presented and discussed in the context of developing low gravity experiments, establishing a detailed property database for the glass materials, and implications for development of new glass and nanocrystalline materials.

**Keywords: oxides, oxynitrides, liquids, containerless, structure.**

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## MICROGRAVITY STUDIES OF LIQUID-LIQUID PHASE TRANSITIONS IN ALUMINA-YTTRIA MELTS

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This research concerns the behavior of molten pseudo-binary alumina-yttria (A-Y,  $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ ) materials under highly non-equilibrium conditions. These oxides form liquids that have a highly non-Arrhenian temperature-viscosity relationship, some compositions undergo a polyamorphic liquid phase transition to form two immiscible liquids. When the liquid mixtures are quenched, two-phase glasses are formed in which both phases have virtually identical chemical compositions. The A-Y based glasses are of interest for laser and optical applications and they are of fundamental and applied interest in materials science. The overall goal of this investigation is to increase the understanding of phase behavior in oxide liquids, to better understand the nature of liquid phase transitions in the melts, and to investigate the way in which the melt viscosity changes with temperature. Low gravity experiments are of interest because they can access “pristine” and quiescent liquid samples needed to investigate subtle changes in liquid properties. The ground-based flight definition research is being performed in facilities that access the highly non-equilibrium liquid by using containerless techniques. This research has led to new high-dopant content optical glass materials which are being commercialized. Liquids and glasses are being characterized as a function of the process conditions and the viscosity of the liquids is being investigated using stinger and drop oscillation techniques at CRI and in collaboration with scientists at NASA and NASDA. The structure and properties of the glasses are being studied in collaborative investigations using SEM, x-ray and neutron diffraction, <sup>27</sup>Al NMR, thermal analysis, and optical spectroscopy. A model of the liquid structure is being developed.

Main findings are:

1. The undercooling limit for the liquid of the YAG-composition (under containerless conditions) is *ca.* 0.58 times the melting point of the crystal.
2. The phase transition occurs *via* changes in the connectivity of the Al-O and Y-O coordination polyhedra and Y-O coordination which preserve stoichiometry.
3. Processing and composition changes which promote formation of predominantly 4-coordinate Al <sup>3+</sup> ions tend to stabilize single phase glasses.
4. Based on limited viscosity data, the fragility index of the liquids is 0.43-0.65.

**Keywords:** oxide liquid, phase transition, containerless, viscosity, structure.

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**Phase Separation and Self-Assembly of Liquid Crystals and Polymer Dispersions: A Ground-Based Feasibility Study for Microgravity**

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Abstract in Progress

## **RESIDUAL GAS EFFECTS ON DETACHED SOLIDIFICATION IN MICROGRAVITY**

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Many microgravity directional solidification experiments yielded ingots with portions that grew without contacting the ampoule wall, leading to greatly improved crystallographic perfection.<sup>1</sup> Such detached solidification is more likely when the contact angle for the melt on the ampoule wall is high, i.e. non-wetting.<sup>1,2,3,4,5</sup> It has been claimed that impurities increase the contact angle. We are focused here on determining the influence of oxygen on the contact angle of molten InSb, including the advancing and retreating contact angles in addition to the usual “equilibrium” contact angle.

We have created a gas flow system that allows us to control the oxygen partial pressure over a sessile drop of InSb on a horizontal surface. The surface is slowly tilted while videotaping to reveal the contact angles on the two sides of the drop just prior to it rolling down the surface. Thus far, we have learned the following:

- Molten InSb readily forms an oxide layer in the presence of trace amounts of oxygen.
- This oxide contains a substantial amount of Ga, which presumably is a trace contaminant that is not detectable in the starting material.
- An infrared filter must precede the video camera in order to produce a sharp image of the drop for later image analysis.
- Tilting the surface on which the drop rests causes the two sides of the drop to display different contact angles, reflecting contact line sticking.
- Vibration strongly accelerates the approach of the drop to its final shape on a horizontal surface by helping to overcome sticking of the contact line.
- Oscillation of the drop surface due to vibration appears to increase as the surface is inclined from horizontal. Presumably, the angle at which the drop rolls down the surface is also reduced by vibration. This observation is particularly significant, as the meniscus must move along the ampoule wall during detached solidification.

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**Keywords: indium antimonide, detached solidification, contact angle, characterization**

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**Identification and Control of Gravity Related Defect Formation During Melt  
Growth of Electro-optic Single Crystals: Silenites  $[\text{Bi}_{12}\text{SiO}_{20}]$ , BSO**

**August Witt**  
MIT

Abstract in Progress

**MELT FLOW DESIGN AND CONTROL IN THE DIRECTIONAL  
SOLIDIFICATION OF BINARY ALLOYS**

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Our main project objectives are to develop computational techniques based on inverse problem theory that can be used to design directional solidification processes that lead to desired temperature gradient and growth velocity conditions at the freezing front at various levels of gravity. It is known that control of these conditions plays a significant role in the selection of the form and scale of the obtained solidification microstructures.

During the first half of this project, a number of melt flow control problems were addressed for directional solidification processes with a sharp freezing front. Various flow mechanisms were accounted in the design process including thermo-solutal, Marangoni and magneto- convection. The examined inverse/design problems were stated as optimization problems in functional spaces with over-specified conditions on the freezing front and incomplete boundary or other process conditions. In the present analysis, we considered as design variables the thermal boundary conditions (furnace design) as well as the magnitude and direction of an externally applied magnetic field. The developed techniques will be demonstrated here with an example of designing the boundary thermal fluxes for the directional growth of a germanium melt with dopant impurities in the presence of an externally applied magnetic field. The design is shown to achieve a stable interface growth at a prescribed desired growth rate. The method will also be demonstrated with the directional growth of a Sb-8.6% Ge melt in an open-boat configuration under the influence of an external horizontal magnetic field such that a stable vertical interface advances with a desired growth velocity.

We will also review current work in progress including extending the present computational melt flow design techniques to multi-phase volume-averaging based solidification models. In addition, we will highlight a computational design framework under development that will allow coupling across length scales with an explicit modeling and design of solidification microstructures using level set methods. Finally, the role that the design techniques being developed may play in the real time feedback control of solidification processes in the presence of uncertainty will be discussed.

**Keywords: computational design, solidification control, inverse problems, fluid flow control, new research**

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## ADVANCED ARC-DISCHARGE CARBON NANOTUBE GROWTH IN SIMULATED MICROGRAVITY: EFFECTS OF GEOMETRY AND ROTATIONS

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The objective of this study is to design, fabricate, and evaluate an arc-discharge set-up that simulates microgravity conditions and exploits the advantages of microgravity for the improved growth of single wall carbon nanotubes (SWCNT). These expected advantages are: (1) the growth of longer tubes with fewer defects and (2) an increased output and efficiency of SWCNT production. Another goal is to achieve selective separation of metallic nanotubes from semiconducting ones.

A major task was solved in the project: the construction of an arc-discharge chamber in which the geometry of the electrodes and the gas flows create conditions simulating microgravity. Contrary to conventional arc-discharge methods, which use two horizontal electrodes, our chamber utilized a large rotating electrode in center surrounded by electrodes from the top, bottom, and sides - thus simulating all possible directions of the gravitational field. The electrode was rotated to obtain a torroidal distribution of plasma. We discovered major differences in the product from these electrode symmetries. The convective flow of plasma and thermal conditions are quite different between horizontal and vertical electrode configurations. In the g-optimized case where the cathode was above the anode, there was a huge “mushroom” shaped deposit on the cathode rod containing 80 % SWCNT's. Deposits in the cathode contained graphitic carbon and multi-walled nanotubes. Long “webs” containing 40-50% SWCNT's formed on the upper walls of the chamber. Low density webs containing 30-40% SWCNT's were found on the bottom of the chamber. The upper part of the cathode rod was covered by a film-type felt contained 50 % SWCNTs. Synthesis of other materials such as N and B and the use of composite catalysts are also in progress.

Nanotubes synthesized by our methods have been used for the initial studies of the photo-acoustic effect upon illumination by light pulses from a Xenon flash lamp. Mass loss as a function of photon flux was measured. We accidentally found that the nanotubes are ignited by a flash of above approximately 3.50 mw/cm<sup>2</sup>, and completely burn away in air. This phenomenon is now being studied in detail.

**Keywords:** Single Wall Carbon Nanotube (SWCNT), g-optimized arc, rotating electrode

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***ID#: 102***

**MEASUREMENT OF CHARGED PARTICLE INTERACTIONS IN SPACECRAFT AND  
PLANETARY HABITAT SHIELDING MATERIALS**

**Cary Zeitlin**

**LBL**

Abstract in Progress